cat

PRACTICAL CHEMISTRY

PRACTICAL CHEMISTRY

BY

JAMES BRUCE

PH.D. (MUNICH), B.SC. (LOND.), F.R.I.C.

ASSOCIATE OF THE ROYAL COLLEGE OF SCIENCE, LONDON, FELLOW OF THE CHEMICAL SOCIETY; FORMERLY HEAD OF THE CHEMISTRY DEPARTMENT OF THE TECHNICAL COLLEGE, HUDDERSFIELD, AND EXAMINER IN CHEMICAL TRADES FOR THE UNION OF LANCASHIRE AND CHESHIRE INSTITUTES

AND

HARRY HARPER

B.SC. (LOND.), A.R.C.S. (LOND.), A.R.I.C.

FELLOW OF THE CHEMICAL SOCIETY

FORMERLY SECOND MASTER, THE BOYS' GRAMMAR SCHOOL, KEIGHLEY

FIFTH EDITION

MACMILLAN AND CO., LIMITED
ST. MARTIN'S STREET, LONDON
1947

Acc-no: 844

COPYRIGHT

First Edition 1910.
Second Edition 1915.
Third Edition 1925.
Fourth Edition 1939.
Fifth Edition 1941.
Reprinted, with corrections, 1945.
Reprinted, with additional corrections, 1947.

cat

541.1
BB3P

PRINTED IN GREAT BRITAIN

PREFACE

DURING many years' experience in teaching practical chemistry to students who have completed a course of elementary work, the authors have felt the need of a laboratory manual more general in character than those commonly used. The preparation of inorganic compounds is a very important branch of experimental work which is too often neglected, but which forms a most valuable preliminary to the study of the analytical methods adopted for the detection and separation of the elements.

In this volume a selection has been made of typical preparations which can easily be carried out by a careful student. The methods described have all been repeatedly practised in the authors' laboratories, and found to yield satisfactory results. A number of simple organic preparations has also been added. While full instructions are given, so as to render it possible for a student of little experience to work by himself, it has been assumed that the work will be supervised by a teacher.

The arrangement of the inorganic preparations is not necessarily that in which they should be taken; this must be left to the discretion of the teacher. But it would be well for a student beginning the study of organic chemistry to work through the organic part in the order given.

Some knowledge of elementary chemistry is expected to be possessed by students using this book. In order, however, to facilitate the work of those who have not much laboratory experience, an introductory section has been included, containing a short account of the apparatus and appliances required for the work which follows, and commonly found in laboratories.

The section on Qualitative Analysis has been made sufficiently complete for most practical purposes, and should be undertaken after the preparation of inorganic compounds. Some knowledge

of organic chemistry, however, will be required for a proper understanding of the reactions and detection of the organic acids.

Quantitative work is dealt with in a simple manner in Part II of the book, and here also a short account of the principles underlying quantitative analysis, and of the apparatus employed in carrying out the work, has been included in the introduction. The sections on Volumetric and Gravimetric Analysis are intended to serve only as a short introduction to these branches of Quantitative work.

It is hoped that the book will be found useful by teachers, and by students preparing for the various University examinations in Practical Chemistry, the examinations of the Board of Education, the Pharmaceutical Society, and other bodies.

J. B.
H. H.

PREFACE TO THE FIFTH EDITION

SINCE the appearance of the first edition the scope of the book has been extended to include sections on electrochemical analysis, the nitrometer and gas-volumeter, gas analysis and the reactions of the less common metals.

In this, the fifth edition, the explanatory articles which found place in earlier issues, on ionisation, the behaviour of solutions, the colloidal state and other topics, have been co-ordinated and extended, and now form a short and consecutive account of the theoretical foundations of analytical chemistry.

The authors gratefully express their thanks to many friends who have helped them with valuable criticism.

They wish also to thank Messrs. L. Oertling & Co. Ltd., for their kindness in preparing a block to illustrate the chainomatic arrangement for balances, Fig. 68.

J. B.
H. H.

CONTENTS

PART I.

PAGE

INTRODUCTION

THE USE OF SOME COMMON LABORATORY APPARATUS AND METHODS - - - - - - - - - 3

SECTION I.

PHYSICAL MEASUREMENTS AND LAWS - - - - - 26

PREPARATIONS

INSTRUCTIONS TO STUDENTS - - - - - - - 113

INORGANIC COMPOUNDS - - - - - - - - 117

CARBON COMPOUNDS - - - - - - - - - 158

SECTION II. QUALITATIVE ANALYSIS

INSTRUCTIONS TO STUDENTS - - - - - - - 256

REACTIONS OF THE CATIONS

THE SILVER GROUP: SILVER, LEAD, MERCURY - - 257

THE COPPER GROUP: MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY, TIN - 260

THE IRON GROUP: IRON, CHROMIUM, ALUMINIUM - 270

THE ZINC GROUP: ZINC, MANGANESE, NICKEL, COBALT - - - - - - - - - - - 276

THE BARIUM GROUP: BARIUM, STRONTIUM, CALCIUM - 282

THE SODIUM GROUP: POTASSIUM, SODIUM, LITHIUM, AMMONIUM, MAGNESIUM - - - - - - 285

PAGE

REACTIONS OF THE ANIONS - - - - - - 288

A METHOD OF ANALYSIS - - - - - - 304

TREATMENT OF INSOLUBLES - - - - - - 318

QUALITATIVE ANALYSIS OF ORGANIC SUBSTANCES - - 319

DETECTION OF ORGANIC ACIDS - - - - - 324

EXAMINATION OF COMPLEX CYANIDES - - - - 327

REACTIONS OF SOME RARE ELEMENTS - - - - 330

SEPARATION OF THE RARE ELEMENTS - - - - 349

PART II.

INTRODUCTION - - - - - - - - - 355

THE BALANCE - - - - - - - - - 356

VOLUMETRIC APPARATUS - - - - - - - 365

SECTION I. VOLUMETRIC ANALYSIS

ACIDIMETRY AND ALKALIMETRY - - - - - 369

INDICATORS - - - - - - - - - 371

BUFFERING - - - - - - - - - 374

STANDARD ACIDS AND ALKALIS - - - - - 376

POTASSIUM PERMANGANATE - - - - - - 390

POTASSIUM DICHROMATE - - - - - - - 399

IODINE AND THIOSULPHATE - - - - - - 402

SILVER NITRATE - - - - - - - - 409

POTASSIUM CYANIDE - - - - - - - 411

POTASSIUM THIOCYANATE - - - - - - 412

PHOSPHORIC ACID - - - - - - - - 414

HARDNESS OF WATER - - - - - - - 415

ESTIMATION OF SUGARS - - - - - - - 418

PAGE

SECTION II. GRAVIMETRIC ANALYSIS

GENERAL OPERATIONS - - - - - - - - 422

ESTIMATION OF SOME COMMON CATIONS AND ANIONS - 428

SEPARATIONS - - - - - - - - - - 456

ELECTROCHEMICAL ANALYSIS - - - - - - 471

THE NITROMETER AND GAS-VOLUMETER - - - - 477

GAS ANALYSIS - - - - - - - - - 481

APPENDIX - - - - - - - - - - 488

INDEX - - - - - - - - - - - 498

PART I

INTRODUCTION

1. Glass tube. It is necessary frequently to cut and bend glass tube in the fitting up of apparatus. For connections, soft glass, that is, readily fusible glass, of small diameter, is generally employed. To break this, make a cut with a sharp file at the required position ; hold the tube firmly in both hands, pressing the thumbs together on the glass opposite to the cut, and pull the hands apart. The tube will break evenly at the cut. For wider tube this will be found difficult ; it is better to make a deep cut on one side of the tube, and apply to it a red-hot point of glass. The tube will crack all round, or partly so. In the latter case, apply the hot point to

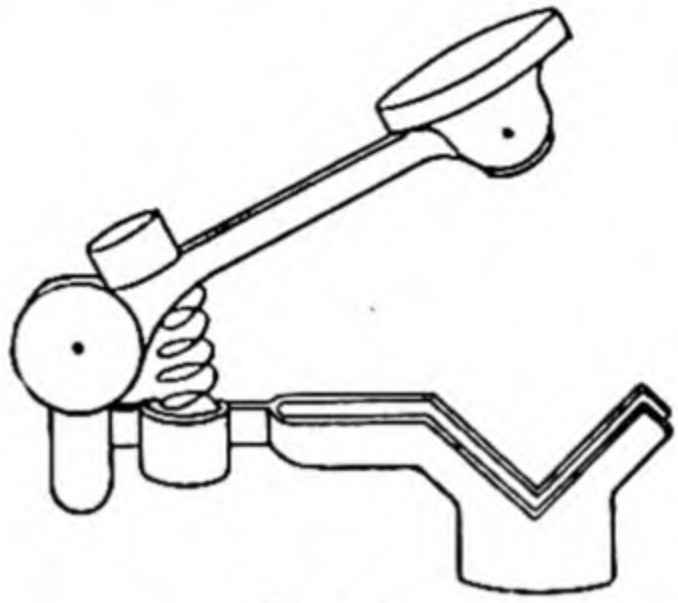


FIG. 1.

the end of the crack and so lead it all round the tube. The glass-cutter (Fig. 1) is very effective for glass tube of all kinds. By rotating the tube in the,cutter, the edge of the steel wheel makes a circular cut, and with this even hard combustion tube can easily be broken.

2. To bend glass tube. Hold the tube in the upper part of the flame of a fish-tail burner, and in the same plane with it, and rotate the tube slowly and continuously on its axis, so that it is uniformly heated (Fig. 2, *a*). When it becomes soft, remove it

from the flame and bend it to the required angle. The bend should then appear as Fig. 2, *b*. If the tube is heated in a Bunsen burner, only a short length becomes softened, and it then bends like Fig. 2, *c*. This is much weaker than the proper bend, and is liable to break under a slight stress.

To draw out glass tube to a capillary, the tube is first softened in the Bunsen burner, with continued rotation, then removed from the flame and the two portions drawn apart until the capillary is of the required diameter. If the capillary is to have a thick wall, the tube must be kept soft in the flame, before drawing, until the wall has thickened sufficiently.

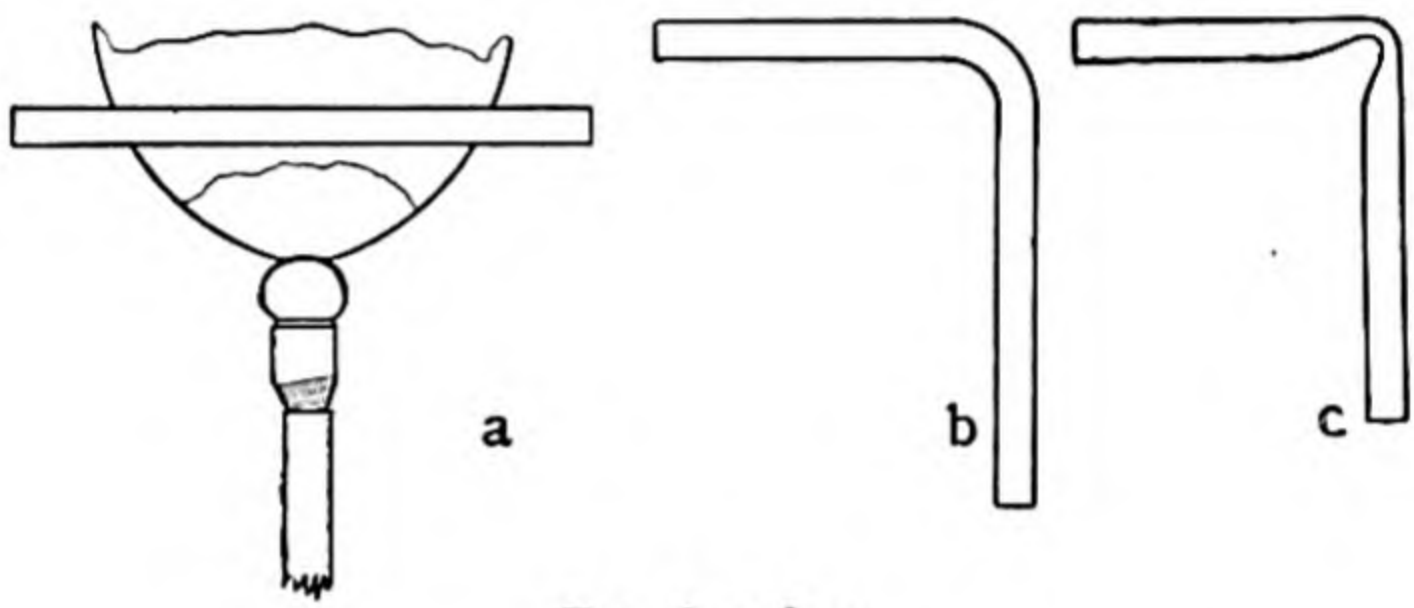


FIG. 2, *a*. *b*. *c*.

To seal the end of a tube, it is best to draw off a portion as just described, and then, in a small flame, draw off the narrow portion where the narrowing just begins. In this way the inside of the tube is kept free from moisture.

For hard Jena glass or combustion tube, the blow-pipe flame will be required, and for the hardest combustion tube, the oxy-coal gas flame. The blow-pipe flame may be made much more effective by allowing it to impinge on a vertical firebrick slab, placed just behind the article to be heated. The heat is thus to some extent conserved.

3. **Corks and cork-borers.** Corks should be made of sound bark only. Before use they should be well softened in the cork-press, or by rolling under a flat weight. To bore the cork, a borer should be selected slightly less in diameter than the tube to be inserted. Begin at each end of the cork and bore half-way

through, rotating the borer on its axis and applying only a slight pressure. With a little care the holes will meet midway. Subsequent filing of the hole is not to be recommended, as this seldom gives a gas-tight joint.

Rubber stoppers may be bored similarly, but the hole should be made from one end only. The borer should be a little larger than the hole required, and should be lubricated with caustic soda solution or glycerine. The borer must also be sharp. It may be sharpened by rubbing the outside of the edge with a file, but better results are obtained by using the special sharpener.

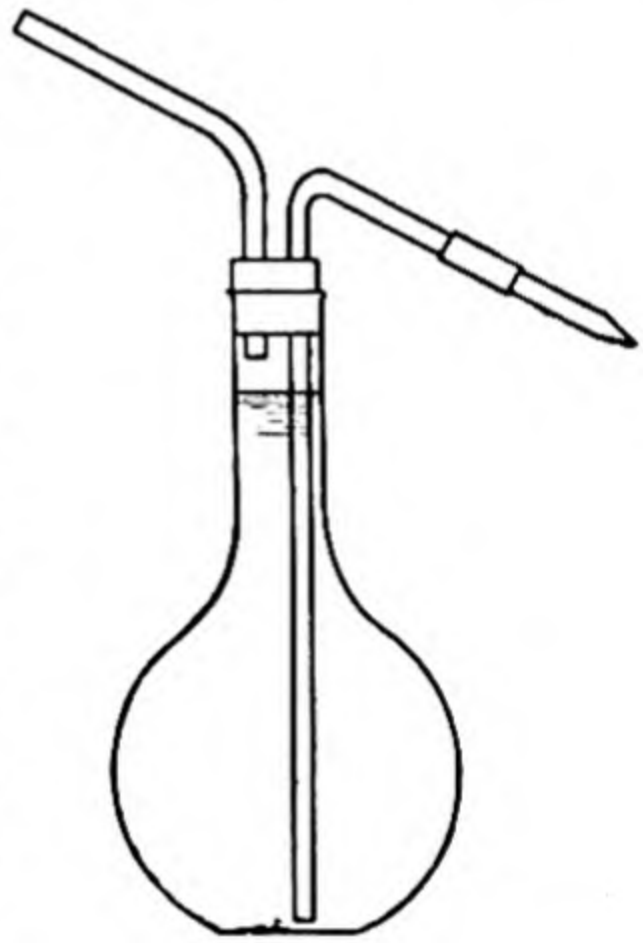


FIG. 3.

4. To fit a wash-bottle. The construction is shown in the diagram (Fig. 3). Rubber stoppers give a more gas-tight apparatus, but should not be used with organic liquids, as alcohol, ether, etc. When using unpleasant-smelling liquids like sulphuretted hydrogen water, a rubber tube may be placed on the end of the glass tube, air blown in and the rubber then closed by the finger and thumb. The stream of water will continue for a short time. The pressure on the tube should be released before again applying the mouth.

SOLUTIONS

5. Preparing a substance for solution. Materials that occur in large crystals should be ground to a more or less fine state of division in a Wedgwood or porcelain mortar (Fig. 4). The process of solution will then be much more rapid, whatever the solvent may be. For hard materials an iron mortar may be used, but there is some risk of contamination with iron, and in quantitative analysis this

FIG. 4.

is to be avoided. Minerals, which must be reduced to an impalpable powder before the treatment with the acid to obtain a solution for analysis, may be crushed to small pieces in the steel crusher (Fig. 5). This consists of three parts. The hollow cylinder fits into the cavity in the base, and the ram fits into the cylinder. The mineral is placed in the latter, and the ram hammered in. The coarse powder so obtained is then very finely ground in the agate mortar (Fig. 6). To obtain the finest powder, a very small quantity is ground at one time, until the gritty sensation can no longer be detected.

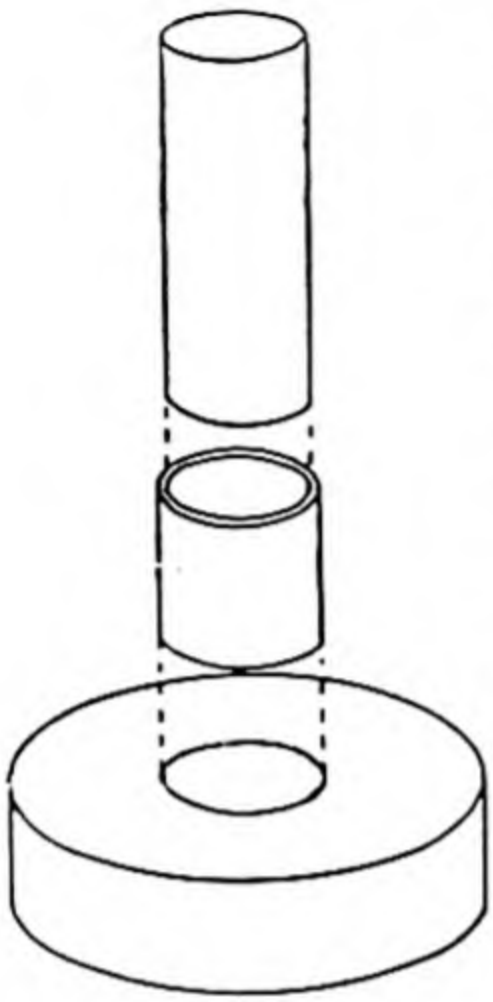


FIG. 5.

6. Making a solution. In general it is sufficient to bring the substance, in a sufficiently fine state of division, and the solvent together in a beaker or flask, stirring or shaking frequently, and heating if necessary on the water-bath. The stirring, if it has to be long-continued, may be effected by means of a water-turbine (Fig. 11), or electric motor.

When a volatile solvent like alcohol or chloroform is being used, the solution should be made in a flask fitted with a reflux condenser, and heated on the water-bath (Fig. 20).

To ensure that a solution is saturated, there must be some of the substance (the solute) remaining undissolved when the operation is over.

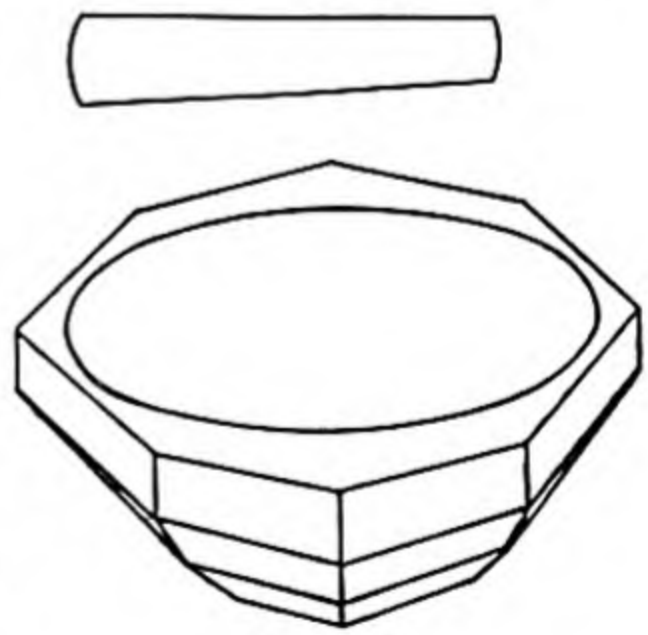


FIG. 6.

SOLUBILITY

7. The solubility of a substance varies with the temperature, increasing in the majority of cases with increase of temperature. All determinations must, therefore, be made

at a definite temperature, which must be kept constant while the solution is being prepared.

The **thermostat** is an apparatus for this purpose. It consists of a water-bath of sufficient magnitude, the water being kept gently moving by means of a current of air from a tube let down to the bottom, or by some form of mechanical stirrer. The temperature is kept constant by interposing a **gas-regulator** between the gas-tap and the burner. There are many forms of regulator. A simple one, Reichardt's, is shown in Fig. 7. The bulb of mercury is clamped in the bath. The gas passes in at *a*, enters the opening at the bottom of the hollow ground-in stopper, and passes from the latter at *b* to the burner under the bath. Should the temperature rise, the mercury expands and partially closes the sloping opening at the bottom of the stopper, thereby diminishing the gas-supply and lowering the flame. A fall of temperature results, with opposite effects. In this way the temperature of the thermostat can be kept within very narrow limits, say half a degree, this depending on the construction and sensitiveness of the regulator, size of bath, etc. For different temperatures the amount of mercury is varied by means of the brass screw at *c*. A small by-pass prevents extinction of the flame.

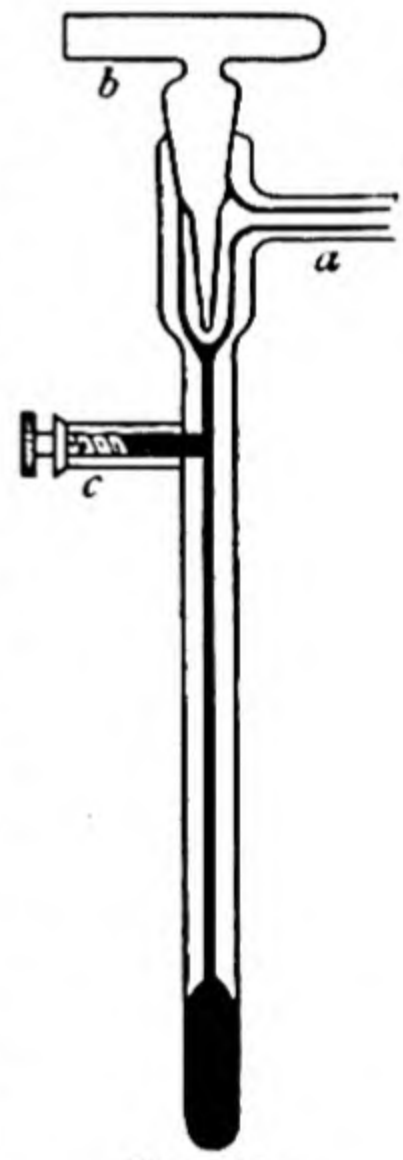


FIG. 7.

This regulator is not very delicate owing to the small volume of mercury and the consequent small expansion when heated. For greater accuracy, regulators have a large bulb filled with toluene or xylene. The expansion of the liquid moves a mercury thread which acts as a " cut off ".

Instead of heating the bath by gas, an electric lamp or an electrical heating unit can be used. When the required temperature is reached, the mercury makes connection between platinum wires and brings into action a small relay which cuts out the heating source.

For high temperature baths, the expansion of air or of a metal

rod, or the change in curvature of a compound metal bar can be used to control the supply of heat.

8. To determine solubility. The material to be examined is placed, together with the solvent, in a flask or bottle, which is then closed, immersed in the thermostat, and frequently shaken

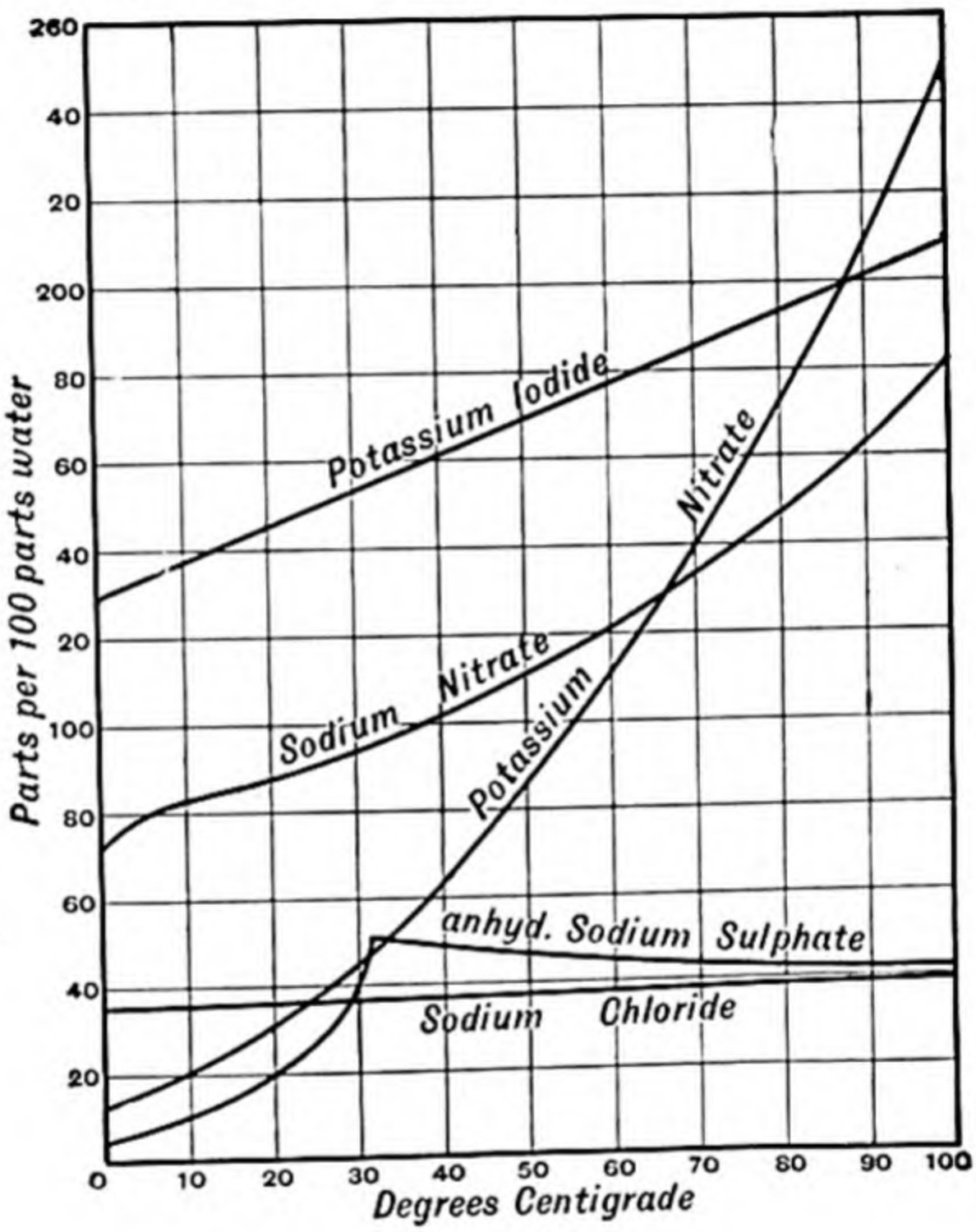


FIG. 8.

or kept in motion mechanically. After an hour or more a portion of the clear liquid is poured into a weighed, stoppered bottle, allowed to cool and weighed. The amount of dissolved substance is then determined by a chemical analysis, or by evaporating and weighing the dry residue.

The relation of solubility to temperature may be shown graphically by means of curves like those in the diagram * (Fig. 8).

* The data for these curves are taken from Comey's *Dictionary of Chemical Solubilities* (Macmillan and Co. Ltd.).

Nearly all exhibit a regular increase, the curves for sodium chloride and potassium iodide being almost straight lines. Sodium sulphate as decahydrate attains a maximum solubility at 33° and then that of the anhydrous salt diminishes (113).

As an example, determine the solubility of potassium dichromate at various temperatures, and draw the solubility curve. Begin with a solution saturated at 80°–90°, by immersing in a large beaker of water. The gas-regulator may be dispensed with. Decant a portion into the weighing-bottle, allow to cool, weigh, then wash out into a weighed porcelain dish, evaporate to dryness on the water-bath, and heat gently with the naked flame until the weight is constant. Allow the remainder of the liquid to cool, take off portions at 60°, 40°, etc., and proceed as before. From these weights the solubility may be calculated at once in grams of dry solid per hundred grams of water.

CRYSTALLISATION

9. From the above solubility curves it is obvious that if a solution, say of potassium nitrate, saturated at 80°, and containing therefore 172 g. of solid per 100 g. of water, be cooled to 20°, the liquid then retains only 31·2 g. per 100 g. of water. A quantity of nitrate therefore, 140·8 g., must separate from the liquid. This separation of a dissolved substance on cooling a solution saturated at a higher temperature generally takes place in forms of definite shape, called crystals, and the process is called crystallisation.

10. Purification by crystallisation. If the original substance contains a soluble impurity, this may be wholly or partly removed by crystallisation. If the impurity does not saturate the liquid at the lower temperature, it will all remain in the mother liquor, and the crystallised substance will therefore be free from it. The degree of purification thus depends on the amount and solubility of the impurities, and repeated recrystallisation is sometimes necessary to obtain a pure product.

In cases where a substance is much less soluble in the cold than in the hot solvent it may be obtained in the form of very small

crystals (" meal ") by rapidly cooling a hot saturated solution, stirring or shaking meanwhile.

11. Fractional crystallisation. In the case of two substances of different solubilities, the less soluble will crystallise first, with only a small amount of the more soluble. A solution, made from the product thus obtained, will by a second crystallisation yield a less impure substance. The product should always be tested for the more soluble substance, and if this is found, the process should be repeated.

By fractional crystallisation, substances having similar solubilities may be separated if one is present in much larger quantity than the other.

A separation may often be effected by pouring off the liquor from the first crop of crystals, before it has cooled to the temperature at which it is saturated with the second substance. The latter will then crystallise on further cooling, together with some of the first substance.

The table of solubilities given in the appendix will be found useful in the above operations.

Certain substances crystallise together in the form of double salts, e.g. ferrous sulphate with ammonium sulphate to form ferrous ammonium sulphate, $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$. Such compounds cannot be separated by this method.

12. Isomorphism. Substances of similar chemical constitution, having an equal number of atoms in their molecules, and crystallising in the same form, are termed **isomorphous**. They often have certain elements in common, and show analogous properties. Such substances have also the property of mixed crystallisation, that is, the crystals separated from a solution of two such bodies contain a mixture of the isomorphous compounds, even when the concentrations of the two bodies in the solution differ considerably. Such compounds, therefore, cannot be separated by crystallisation.

The law of isomorphism was discovered by Mitscherlich in 1820, by an examination of the corresponding salts of phosphoric acid, H_3PO_4, and arsenic acid, H_3AsO_4. Examples will be given later, in the alums, etc.

13. Growth of crystals. By slow evaporation of the solvent

larger and purer crystals are obtained. This may be effected in a shallow flat-bottomed crystallising dish (Fig. 9). The small crystals which separate first from a solution are usually perfect. If such crystals are suspended in the saturated solution by a hair or silk fibre, or if they are turned every day on different faces, so that all are equally exposed to the action of the solution, large and perfect crystals can readily be obtained. In a crystalline mass, however, the individual crystals are usually incomplete or distorted.

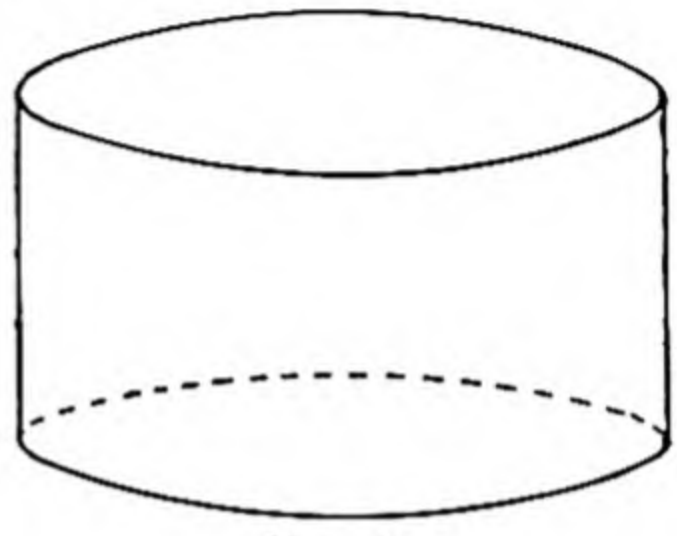


FIG. 9.

PRECIPITATION

14. When solutions are mixed containing two bodies which can, by interaction, produce another substance insoluble or sparingly soluble in the solvent, then, in general, this other substance is produced, and separates from the liquid in the form of a **precipitate.** Thus when barium chloride and sodium sulphate are dissolved separately in water, and the solutions mixed, barium sulphate is at once separated as a white precipitate, this being practically insoluble in water.

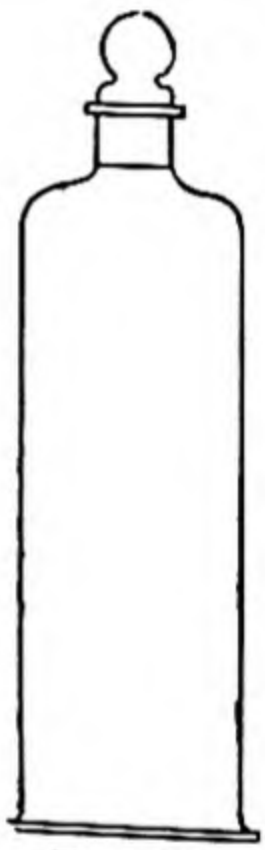


FIG. 10.

Precipitation may take place slowly or rapidly, and is less or more complete, according as the precipitated substance is more or less soluble in the solvent. A change in the composition of the solvent often brings about precipitation or rapid crystallisation, as, for example, in the purification of common salt, by dissolving hydrochloric acid in its saturated aqueous solution, the addition of water to the alcohol in the preparation of iodoform, or the addition of alcohol in the precipitation of lead sulphate. The rate of precipitation is often increased by vigorous stirring or shaking in a tightly stoppered precipitation jar (Fig. 10). In all cases the solution should be constantly stirred while the precipitant is added, to ensure thorough mixing. A large excess

of the precipitant should be avoided, when possible, in order to facilitate the subsequent washing.

When the solubility of the precipitate is not appreciably increased by heating the liquids, it is often advisable to do this; the result is to render the precipitate more granular. Many precipitates also which are produced at first in a gelatinous form, as magnesium ammonium phosphate from strong solutions, become

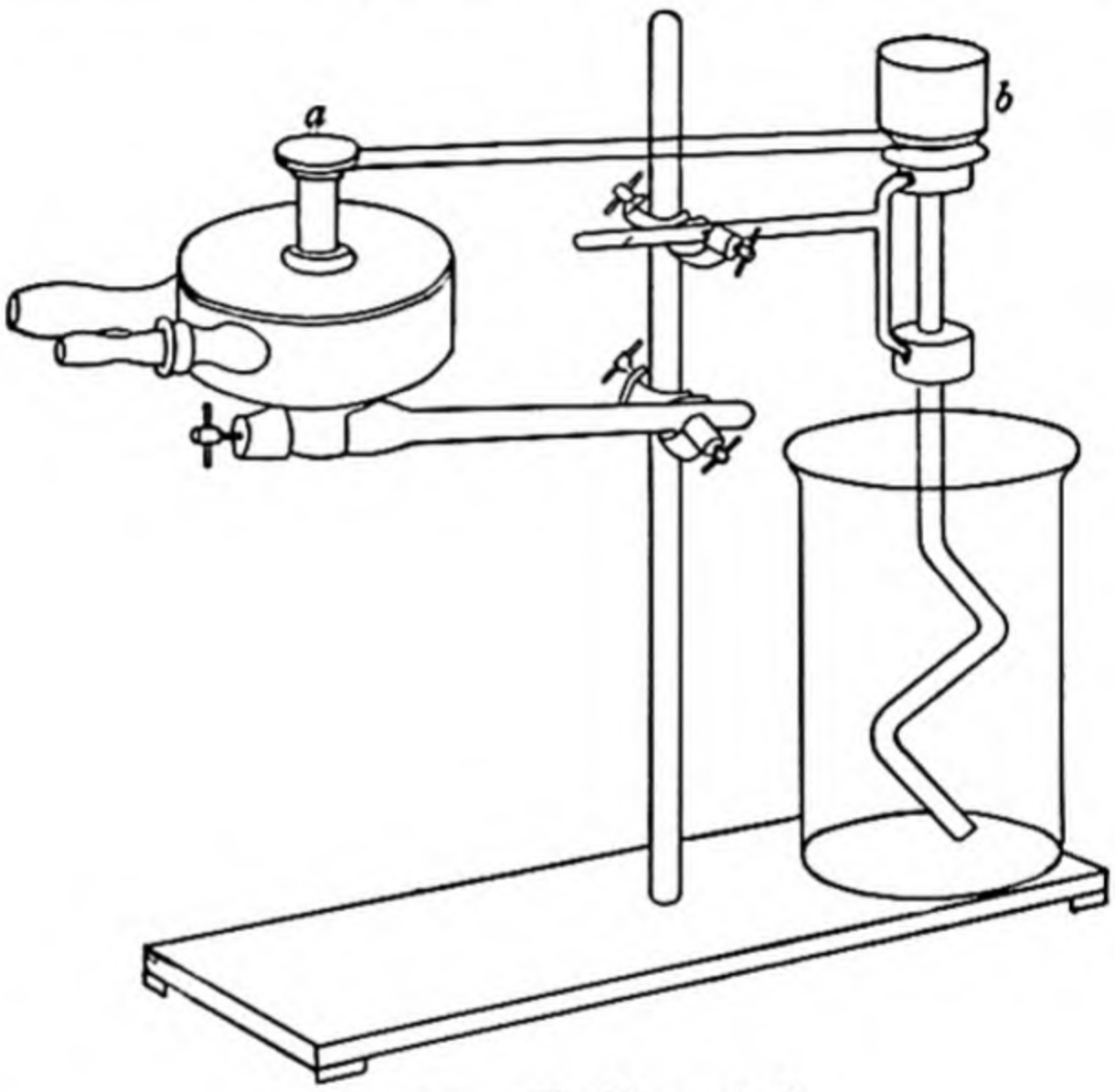


FIG. 11. (Turbine, etc.)

crystalline on standing for some hours. This is very important with regard to the subsequent filtration, as a crystalline or granular precipitate is always more easily and rapidly filtered and washed than one of a gelatinous or coherent nature.

When a large quantity of material has to be dealt with, or when the precipitation occupies some time, the stirring or shaking may be done by means of a water-turbine (Fig. 11), electric motor or hot-air engine. The first of these is generally available. The small wheel *a* of the turbine is coupled by means of a thin cord or rubber band to the wooden pulley *b*, in which the bent glass rod stirrer is firmly fixed.

FILTRATION

15. Before filtering off a precipitate it is in general advisable to allow it to settle, and to filter the clear liquid first. The precipitate may then be washed by **decantation**, that is, by mixing it with fresh solvent and again allowing to settle, after boiling if necessary to facilitate the removal of the impurities.

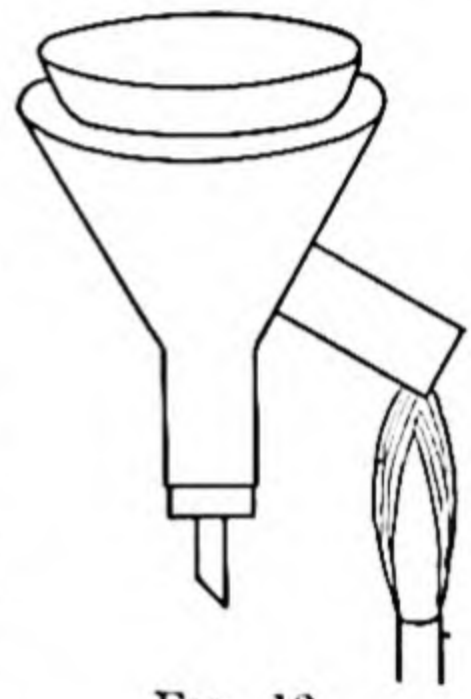


FIG. 12.

For the large quantities of liquid employed in preparations, a cloth bag filter may be used, made of stout calico and supported on a wood frame. It is also useful to employ a **fluted** filter of paper. This is made by folding the paper into 8, 16, or 32 folds according to the size of paper, instead of 4, and then arranging the folds alternately inwards and outwards. The filter is thus arranged in a series of ridges meeting at the apex. This ensures more rapid filtration.

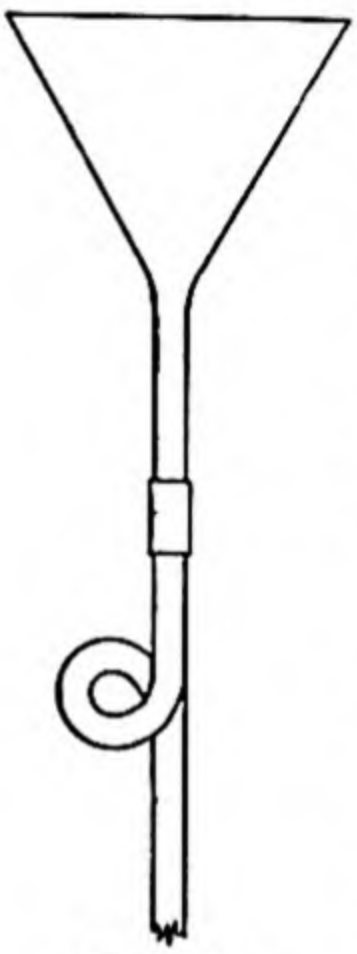


FIG. 13.

When it is desirable to filter a hot, nearly saturated solution, the filter funnel must be kept hot to avoid crystallisation of the substance. This may be done by placing the funnel in the hot water jacket (Fig. 12), passing the stem through a good cork in the bottom of the jacket.

Filtration may be hastened in several ways. In analysis it often saves time to place a small fall-tube (Fig. 13) on the end of the funnel. This can easily be made by softening a glass tube in a large flame and then bending it into a complete circle. The lower straight piece should be six or seven inches long, the upper one short.

16. Filter pumps are commonly used to accelerate filtration. The upper end of the pump (Fig. 14), which may be of glass or metal, is firmly connected to the water-tap by means of strong pressure tube, secured by copper wire. The water issues through the narrow jet *a*, and at a high speed enters the slightly wider

upper end of the lower tube, forcing the air down this tube in its flow. The bendings in this tube are intended to obstruct the backward passage of air. A diminished pressure is thus created in the bulb of the pump, and in any vessel connected with it by means of the side tube. These pumps are very useful for vacuum distillation, and the pressure can readily be reduced to 10-12 mm.

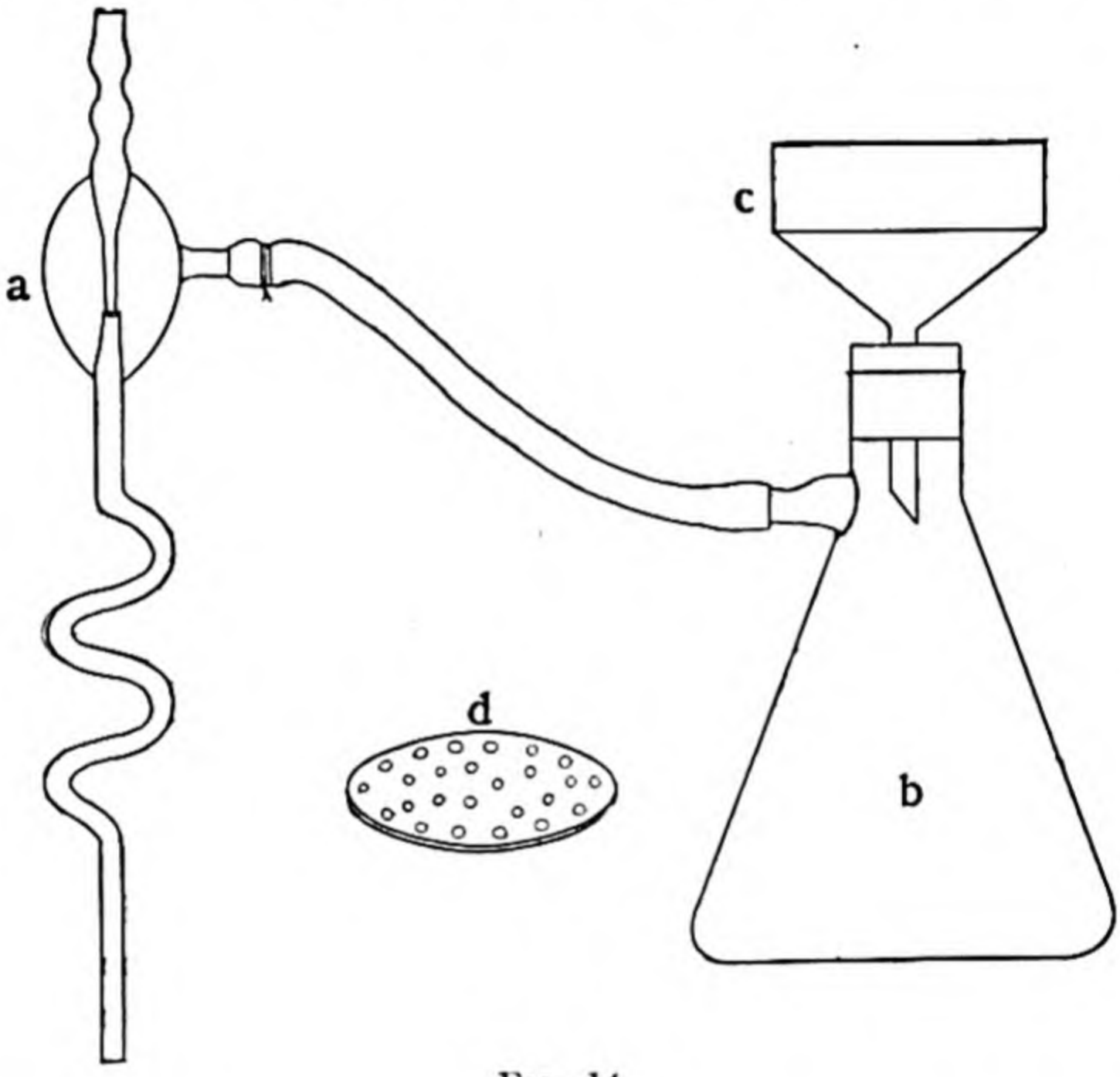


FIG. 14.

The pump flask *b* shown in the diagram is of strong glass, and the Buchner funnel *c* is made of porcelain, with a flat perforated bottom which is either of one piece with the funnel or detachable. An ordinary glass funnel may be used, and the perforated porcelain plate *d* inserted.

The perforated bottom or plate is covered with filter paper or linen, cut to the required shape. This is then moistened with water, and pressed down so that the edge is completely closed. The pump should be working slowly while this is done. To stop

the pump when filtration is over, *first detach the tube* from the pump flask, and then turn off the water. If the water is first turned off, some may run into the pump flask on account of the low pressure therein.

For the filtration of certain mixtures, filter paper is unsuitable, and linen cloth, glass wool or asbestos (see Gooch crucible) can be used. A very convenient filtering device for many purposes consists of a disc of glass (Fig. 15) which has been ground finely, carefully graded for particle size and the particles fritted together with great care to ensure uniform size of the pores in the disc. The disc is then fused directly into a funnel or container (Fig. 16).

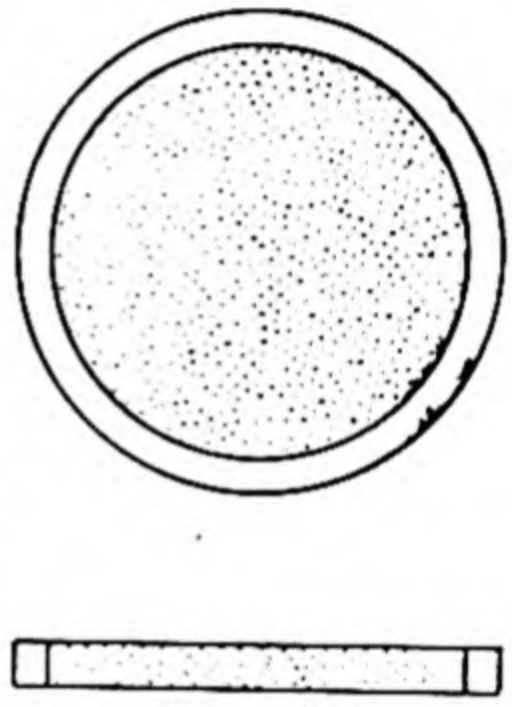


FIG. 15.

Buchner funnels, Gooch crucibles, silica discs and crucibles, funnels for use in qualitative analysis, micro-analysis, etc., are now made in this way.

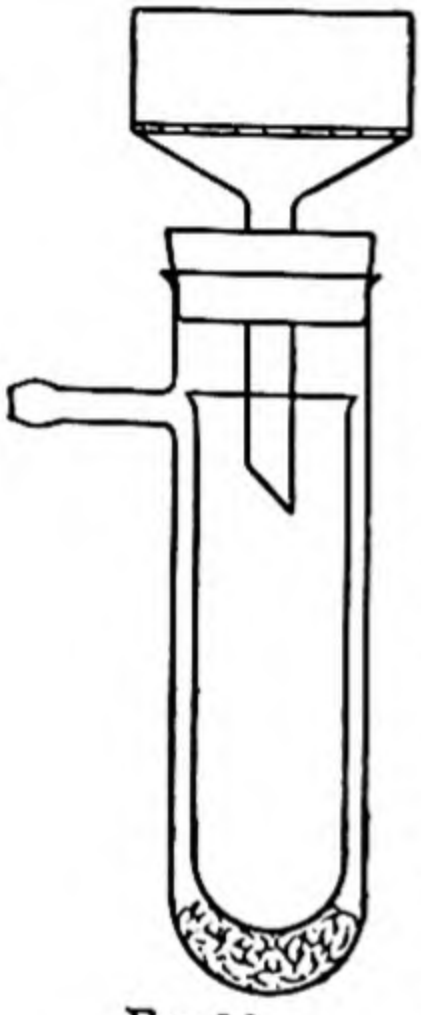


FIG. 16.

Discs are made of various pore size to suit the purposes for which they are to be used.

17. **Washing precipitates.** As already explained, this may be done partially in the precipitation vessel by decantation. The liquid in each washing should be run off as completely as possible before adding the next. This applies also to the final washing on the filter. Suppose that in good and defective working respectively one-tenth and one-half of the liquid is left each time when the next washing is added. Then after three washings the concentration of the impurity is reduced in the first case to one-thousandth, in the second case to one-eighth only of its original value.

When the material to be filtered is soluble, as in the preparation of crystallised salts, the quantity of solvent used for washing must of course be as small as possible.

When the pump is used for filtration, it must not be at work

while the washing is being done. Detach the tube from the pump flask, add the washing liquid to the funnel, and gently mix it with the upper portion of the substance, taking care not to disturb the filter cloth. Then allow the liquid to percolate through the mass by gravitation, and use the pump only to complete the draining. In this way the whole mass of the material is washed by the liquid. If the pump is constantly at work, the washing liquid is simply

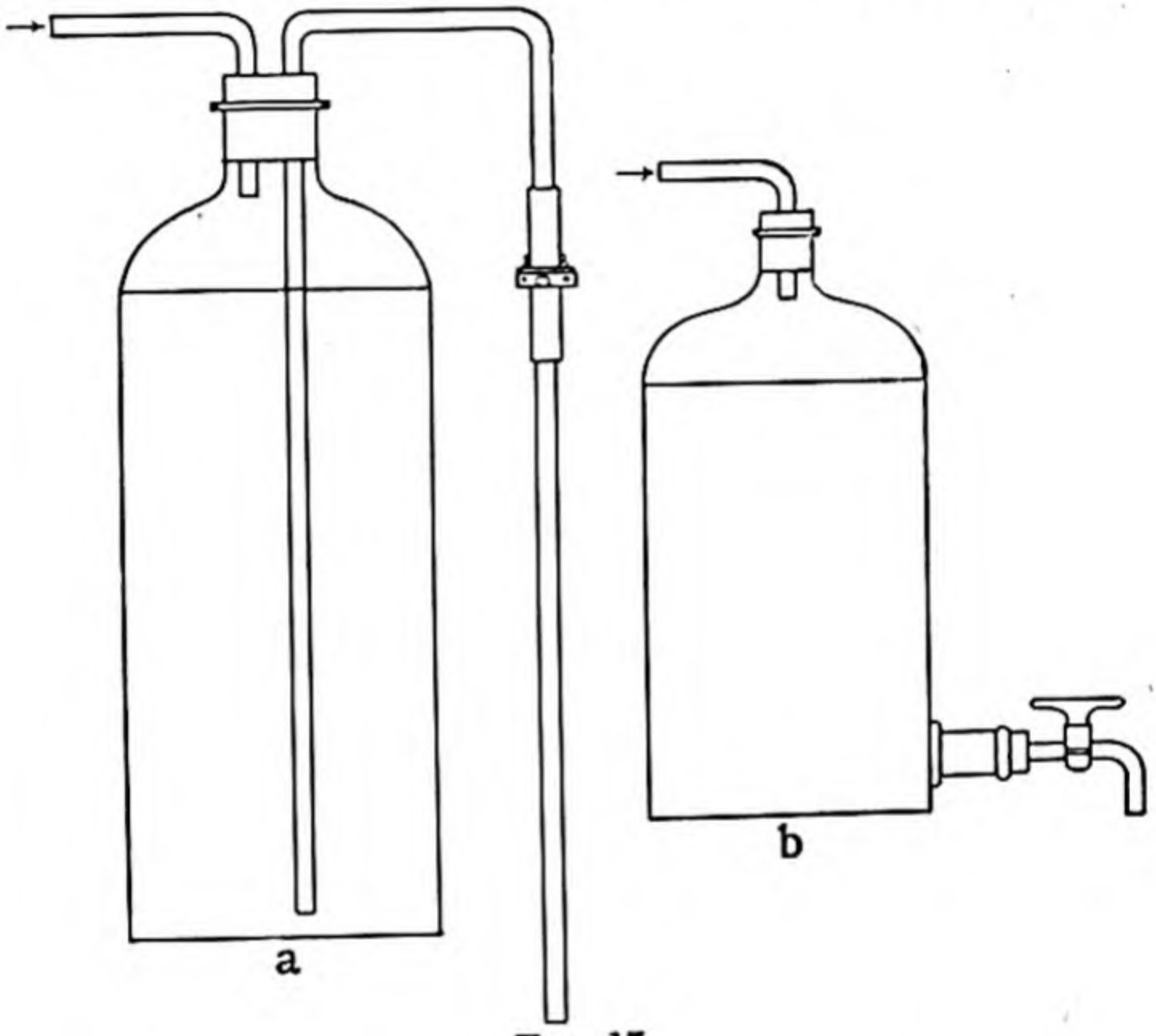


FIG. 17.

drawn through the mass by the easiest route, and the washing is consequently incomplete.

To make the draining off of the liquor as complete as possible, the substance in the funnel may be pressed down by aid of a flattened glass rod, or the top of a flat glass stopper.

ASPIRATORS

18. These are employed for various purposes in which a slightly reduced pressure is required, as e.g. for drawing a current of air

through an apparatus or a liquid, to assist filtration, etc. They are of various forms, some of which are shown in the diagrams. An ordinary glass bottle may be employed (Fig. 17, *a*), fitted with stopper and two tubes. Water is run from the bottle by the longer tube, which acts as a syphon, and air is drawn in by the shorter tube. The second form, *b*, acts similarly, the water being drawn off by the glass tap at the bottom. A small aspirator may be made at once by simply inverting the wash-bottle (Fig. 18),

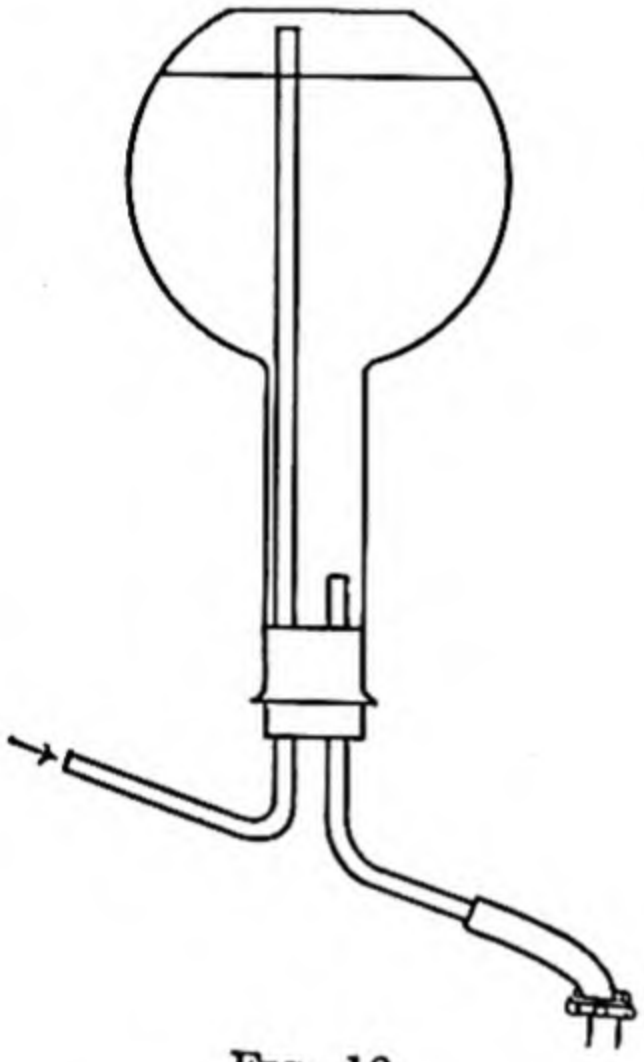


FIG. 18.

FIG. 19.

and allowing the water to run off by the short tube. A screw clip on the rubber tube regulates the flow of the water.

These aspirators are, however, intermittent in action, and not of great power. The most generally useful, and at the same time the most powerful and continuous for ordinary laboratory use, is the water pump already described (Fig. 14).

By means of the water pump also, a current of air under increased pressure may be obtained. The arrangement is shown in Fig. 19.

Water and air together are forced into the bottle by the pump. The water is run off at the bottom, and the compressed air escapes by the side tube at the top of the bottle. This current of air can be made powerful enough to work an ordinary gas blowpipe.

EVAPORATION

19. In many cases a liquid may be evaporated by boiling it in an open vessel, preferably one which gives the liquid a large

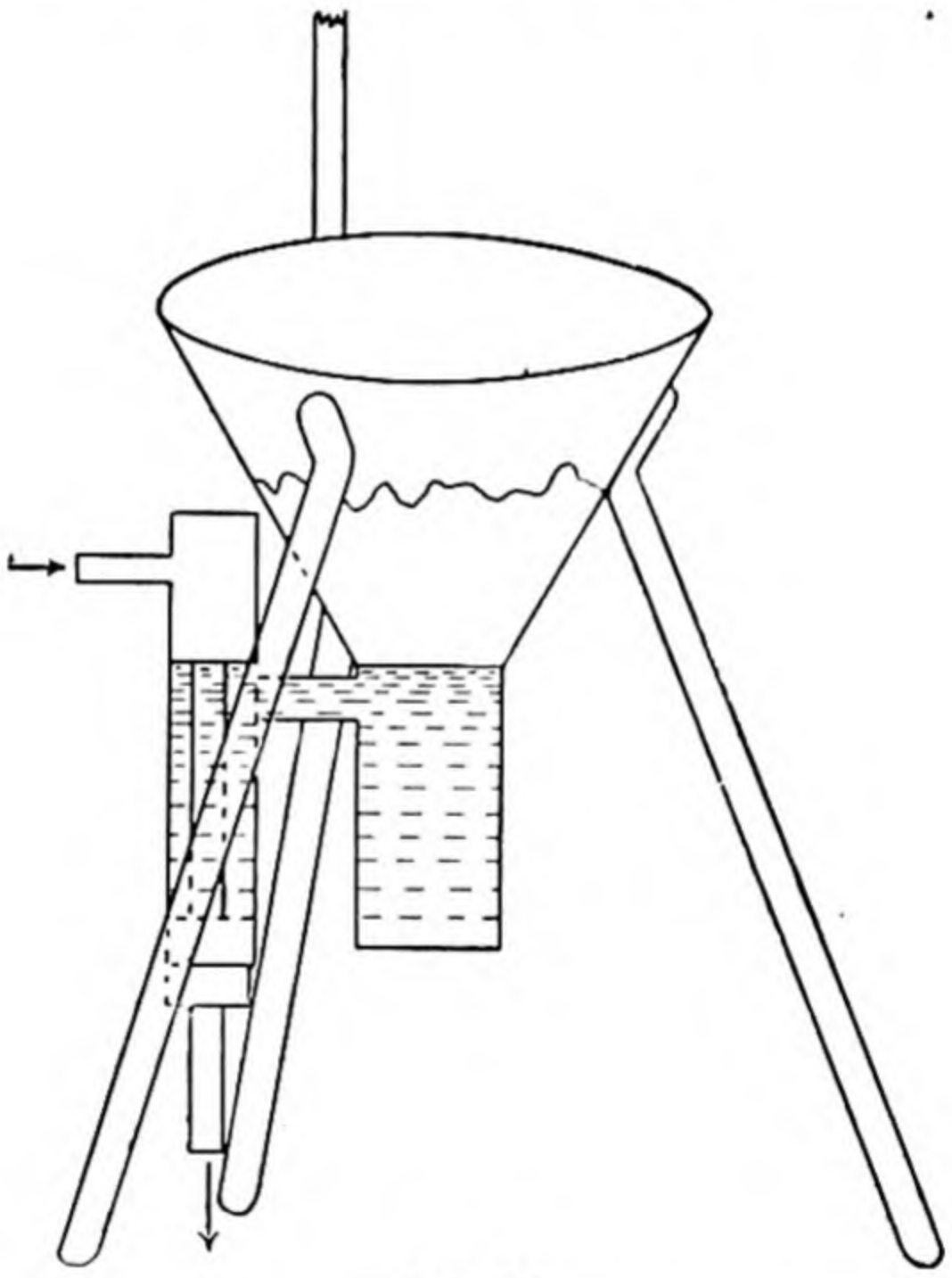


FIG. 20.

surface, without detriment to, or loss of, the dissolved substance. Porcelain dishes are usually employed for this purpose.

Evaporation may also be carried on more slowly, by heating on a steam-bath. A simple steam-bath may be made by boiling water in a beaker, and placing the dish containing the liquid on

the mouth of the beaker. A hot plate heated by gas or electricity is also convenient.

A water-bath, strictly regarded, is one in which the vessel to be heated is immersed in the water. Such baths are often employed, as *e.g.* in determining solubilities as described earlier. But the term is also applied to all kinds of steam-baths in which the steam is generated from water in the same bath.

One of the most convenient forms of such water-baths for the working bench is shown in Fig. 20. As indicated in the diagram, the amount of water required is small, and this admits of rapid heating. The constant-level arrangement at the side obviates the risk of boiling to dryness. A series of concentric rings of copper or porcelain on the mouth of the bath makes possible the accommodation of vessels of different sizes. Lastly, one of the legs is continued in the upright iron rod, on which a clamp may be held for the support of a reflux condenser.

Evaporation may also be carried on by distillation, with condensation of the solvent if this is of value.

When it is desirable to evaporate a liquid rapidly without much increase of temperature, this may be done by distillation under diminished pressure, at the ordinary temperature or a little over it. In this case the liquid is contained in a strong, round-bottomed flask, and a tube drawn to a fine capillary passes into the liquid. For receiver a distilling flask or pump flask is taken, and this is exhausted by the pump, with an interposed empty bottle in case of accident from a back-flow of water. The capillary referred to above admits a stream of minute air-bubbles through the liquid, and secures regular boiling.

The vacuum desiccator (Figs. 21, 22) may also be used for rapid evaporation at the ordinary temperature.

DRYING

20. Desiccators. A desiccator is a vessel in which a dry atmosphere can be maintained, and which can be made gas-tight. It is employed for a variety of purposes. Crucibles are allowed to cool, before weighing, in the desiccator; weighing bottles con-

taining substances for analysis may be kept therein; crystals may be dried, or liquids evaporated, especially in the vacuum form of apparatus. Two forms are shown in Fig. 21, and a third

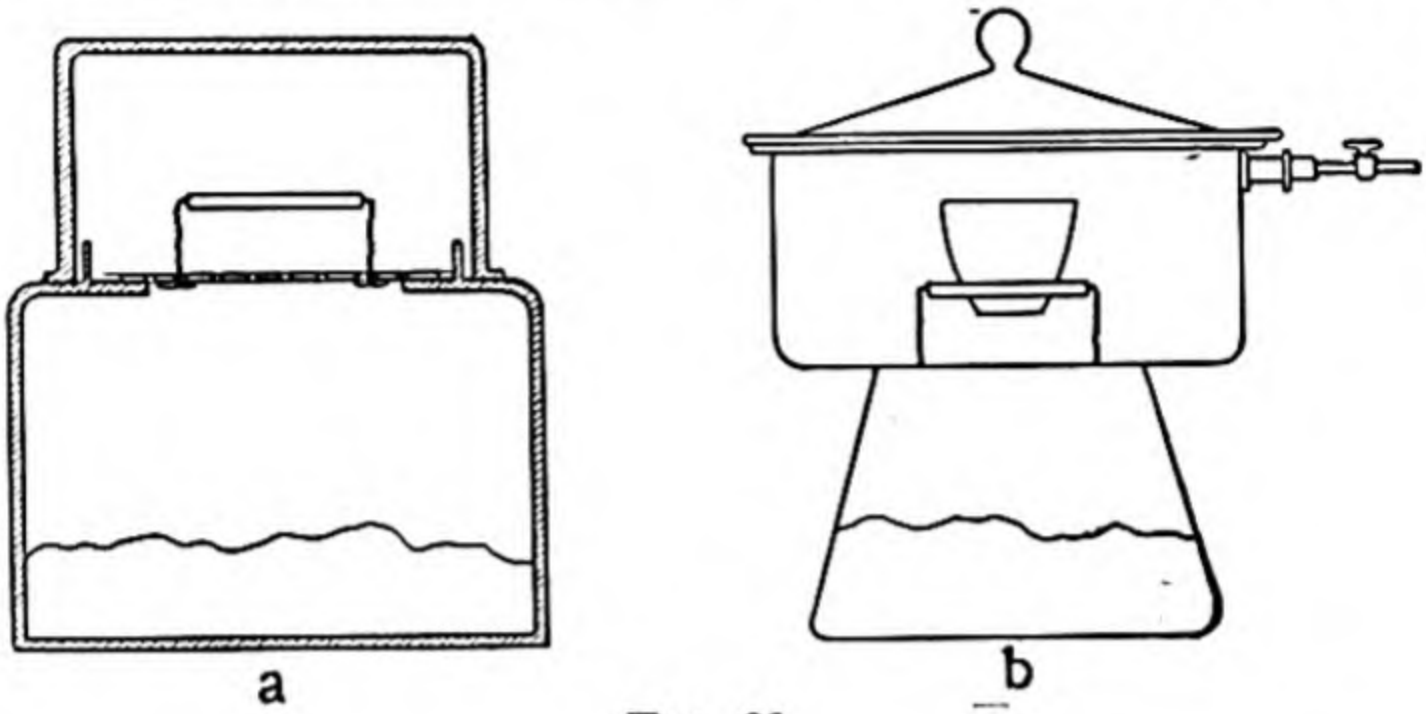


FIG. 21.

in Fig. 22. The drying agent, sulphuric acid, with or without pumice, or anhydrous calcium chloride, is placed in the lower part of the vessel. Calcium chloride is preferable to a liquid, in an

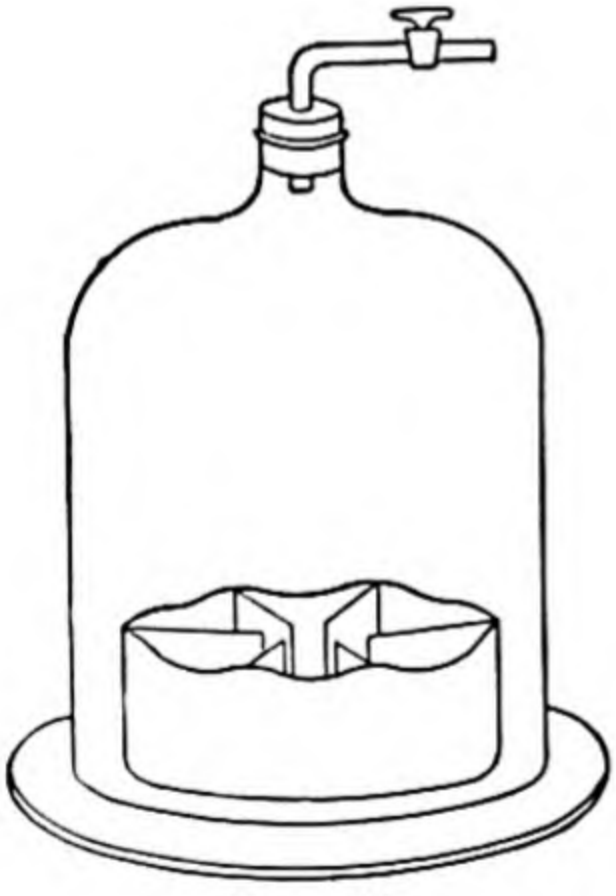


FIG. 22.

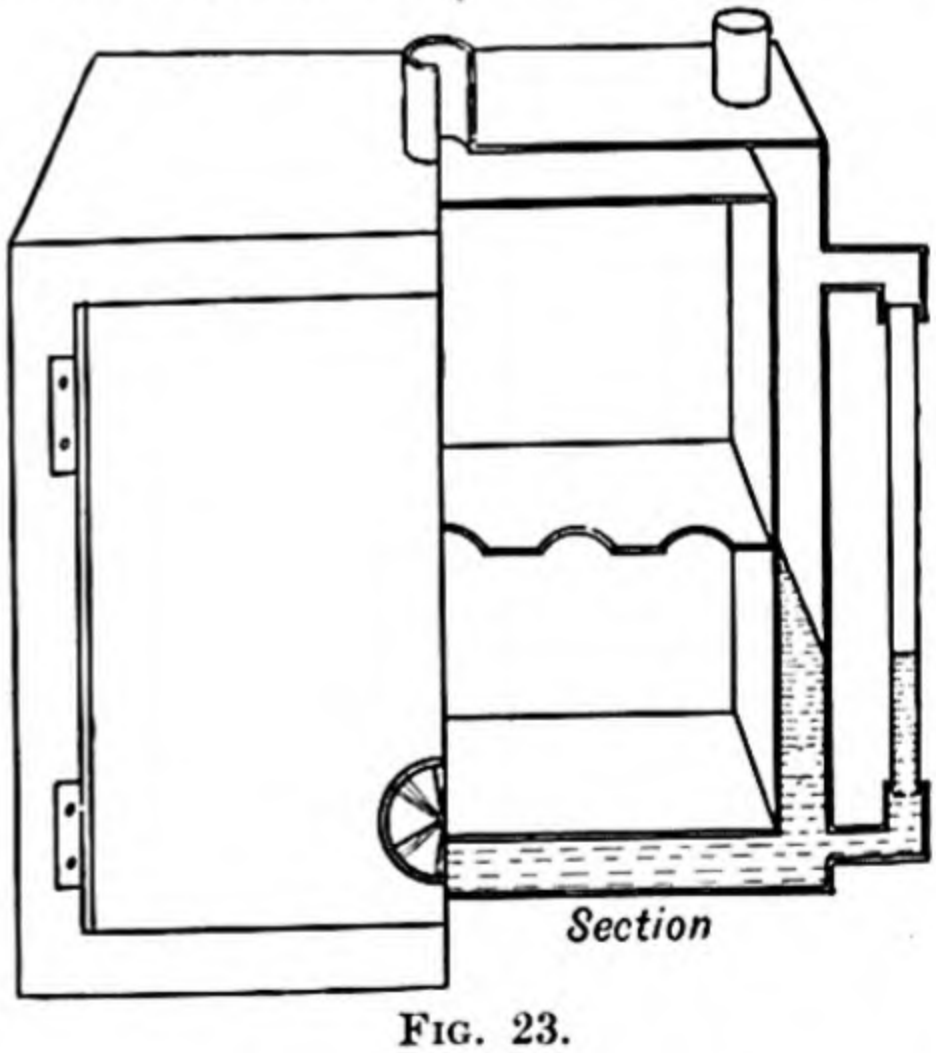


FIG. 23.

apparatus which has to be carried to and fro, and for vacuum desiccators sulphuric acid should not be used. The under edge of the cover is slightly greased. The bell-jar (Fig. 22) has the

lower rim well ground, and stands on a thick ground glass plate. The drying agent is placed in the porcelain trough, on which a dish or crucible may be laid. The bell-jar is closed by a stopper and glass tap, so that, like Fig. 21, *b*, it may be exhausted, and the tap then closed. A good vacuum desiccator should preserve

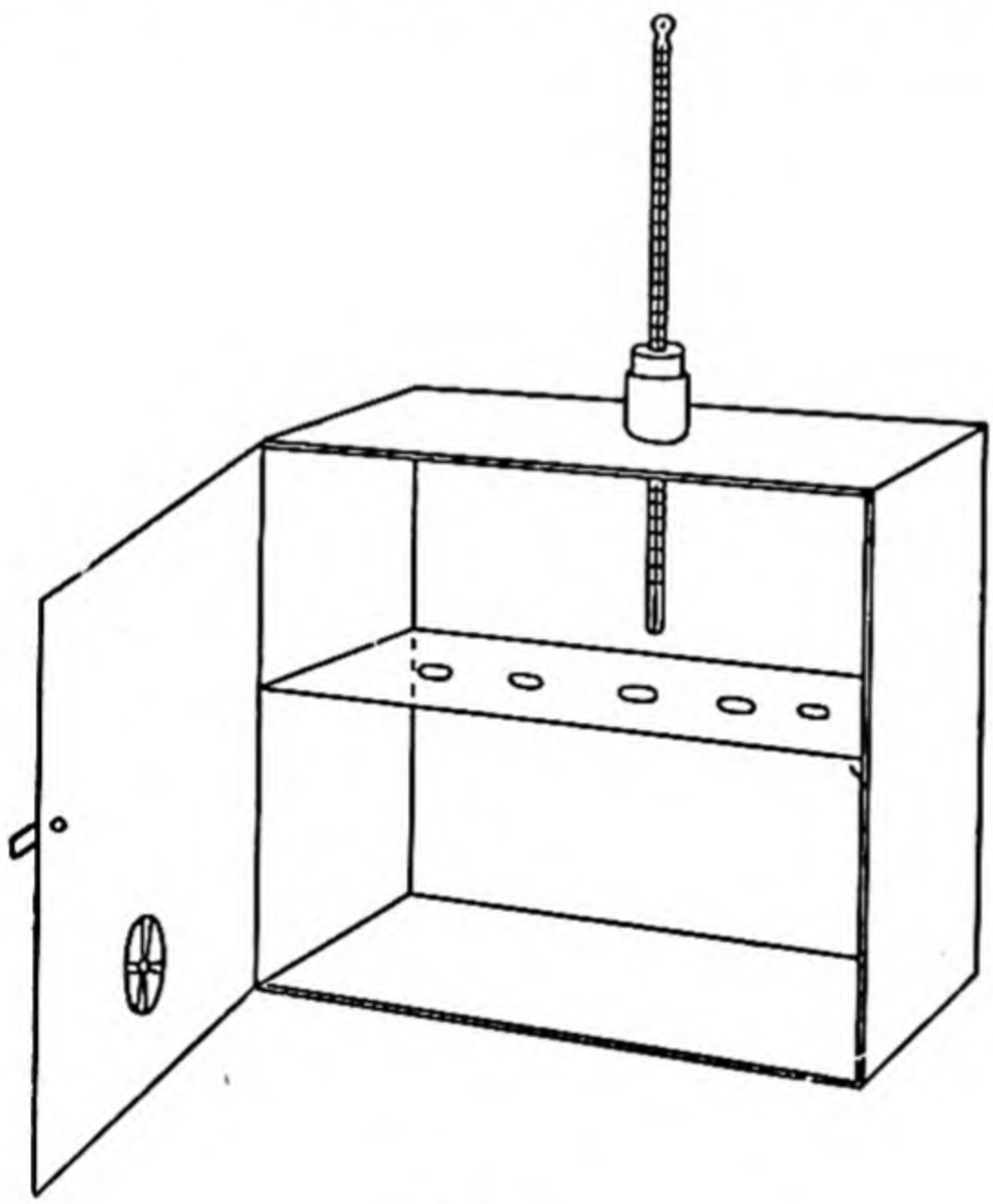


FIG. 24.

the vacuum for several days, but this should be tested, and the exhaustion repeated.

The drying of a solid substance may be assisted greatly by spreading it on a **porous clay plate**, especially if it be finely divided and retentive of moisture. The clay absorbs the water slowly ; the drying may be further accelerated by placing the plate in the vacuum desiccator.

21. Ovens. For drying at higher temperatures, water, steam or hot-air ovens are employed. The construction of a water-oven is shown, partly in section, in Fig. 23. It consists of a double-

walled box, usually made of copper, the water being contained in the space between the walls. The glass gauge at the side shows the level of water. A constant-level device may also be fitted.

The steam oven is of similar construction, the steam circulating through the space between the inner and outer walls. A number

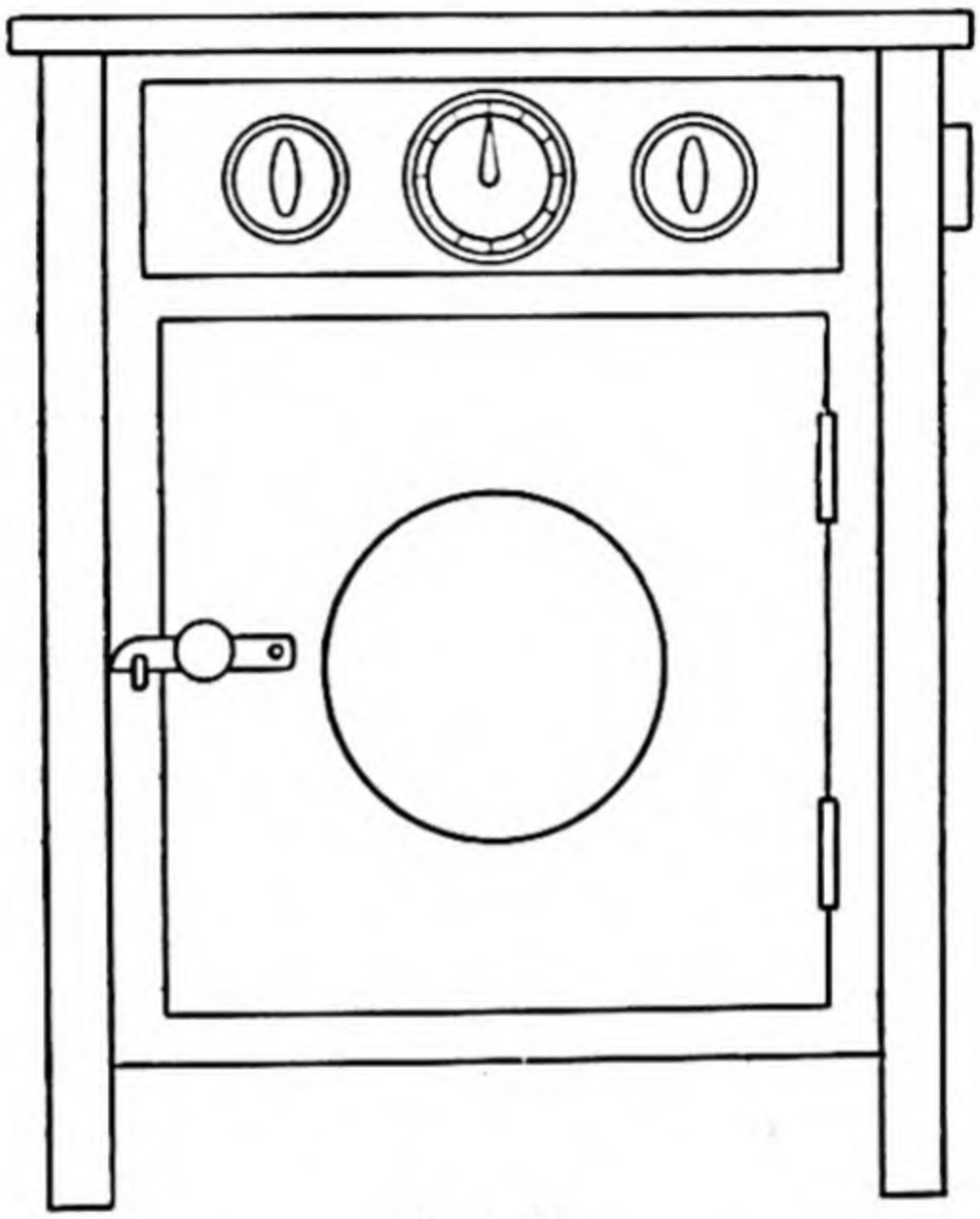


FIG. 25.

of these ovens are generally built together, the steam-space surrounding each compartment.

For temperatures below or above 100°, similar ovens may be used, with other liquids, or hot air may be circulated through the walls.

The air-oven (Fig. 24) need be only a simple box, and is made of sheet copper or iron. The outside is sometimes covered with asbestos board to diminish the loss of heat. A thermometer is inserted in the top, and the temperature may be kept constant if desired by using a thermo-regulator such as that already described (Fig. 7, par. 7).

The electric oven (Fig. 25) is more susceptible of exact control,

and can be kept at any desired temperature between say 50° and 300° by means of a bi-metallic " thermostat ".

Great care must be exercised in the drying of all substances which are affected by heat, as, *e.g.* salts containing water of crystallisation. Such bodies must, in general, be dried at a low temperature.

22. The drying of gases. The operations of washing and drying gases are often carried out in the laboratory, the general procedure being to bubble the gas through the liquids in wash-bottles. An ordinary bottle fitted as shown in Fig. 26, *a*, will serve for this purpose. A ground-in top carrying the two tubes is often fitted. This has the advantage of being entirely made of

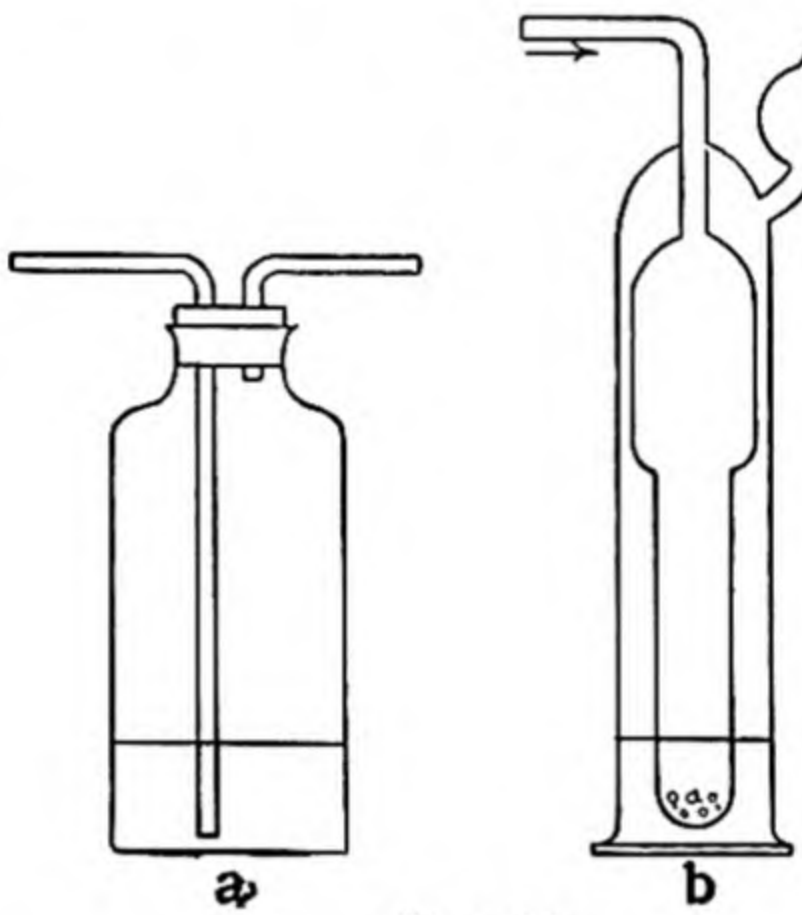


FIG. 26.

glass, but the stopper is sometimes loosened by the pressure of gas. A better form is the Drechsel wash-bottle (Fig. 26, *b*), which is all of glass and in one piece. The entrance tube is widened inside, so that in the event of a back-pressure the liquid cannot reach the upper part of the tube.

Water may be used for removing soluble impurities from gases which are themselves sparingly soluble in water. If the gas is soluble in water, its saturated solution may be employed to wash it. For drying, sulphuric acid is generally useful.

To ensure efficient washing or drying, however, it is not enough to use wash-bottles in this manner. The gas should be passed through large U-tubes (Fig. 27) which are filled with chips of pumice or glass beads, drenched with water for washing, or with sulphuric acid for drying. Calcium chloride may be used for drying most gases. For ammonia, caustic potash or quick-lime in small pieces is used, and these may be placed in a drying tower (Fig. 28), resting on the perforated lead plate. For more complete drying, phosphorus pentoxide is used, and should be dusted over the glass beads in the U-tube, so that the passage does not become stopped by the pasty metaphosphoric acid. Magnesium perchlorate is an excellent drier. The trihydrate, $Mg(ClO_4)_2 3H_2O$, is as efficient as P_4O_{10}. It loses the water at 250°, forming the anhydrous perchlorate, known as "anhydrone". The latter is much more efficient than P_4O_{10}, and may

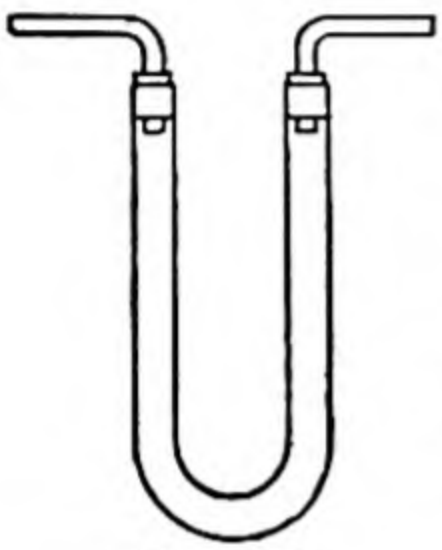


FIG. 27.

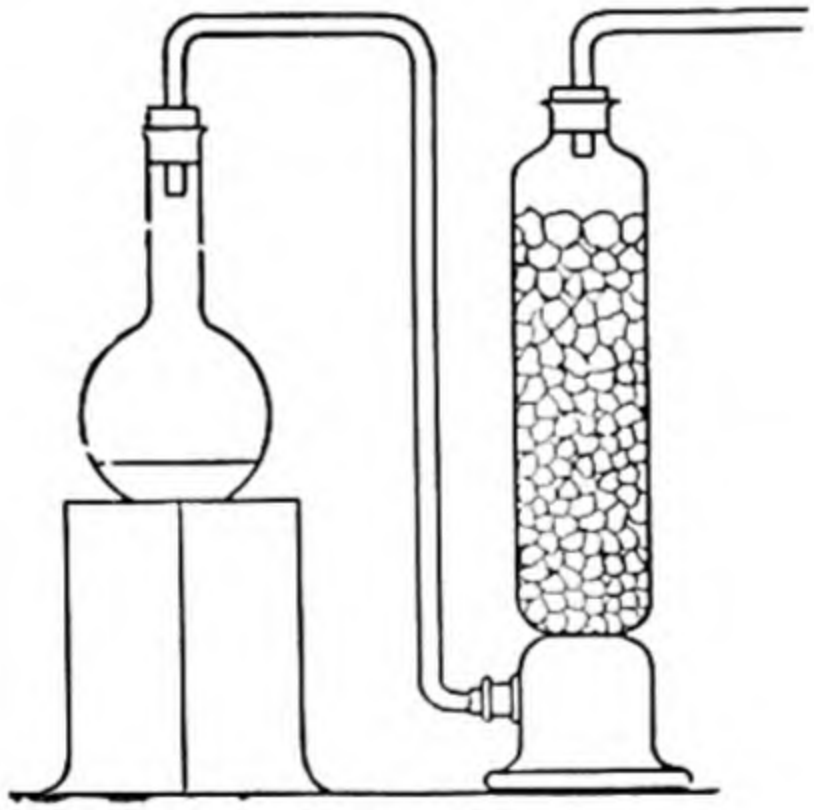


FIG. 28.

be used for basic or neutral gases. It should not be used for acid vapours, which may liberate perchloric acid; this is liable to explode (Laby. precautions, 3). Active silica gel also is being increasingly used as a desiccating agent, and is obtainable in a convenient form for drying the air in balance cases. Perchlorate

and silica gel can both be regenerated after use by heating in an oven.

23. The separation and drying of liquids. Liquids can be separated (*a*) by fractional distillation (48), (*b*) by steam distillation (45), or (*c*) by salting out, *i.e.* by dissolving some substance in one of the liquids so as to render that liquid much less soluble in the other. Immiscible liquids can be separated by decantation, or better, by the use of a tap or separating funnel (Fig. 29). The mixture is poured into the funnel and allowed to settle, and the lower liquid is run off.

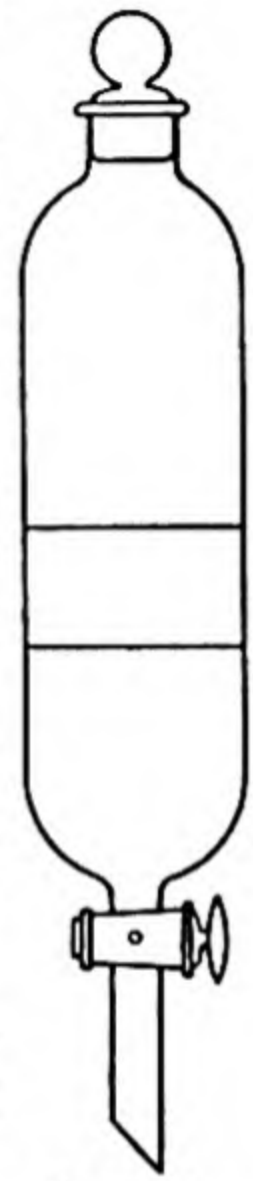


FIG. 29.

Liquids can be dried by the use of the above or other materials, the liquid and the desiccating agent being placed together in a dry flask, which is then corked and allowed to stand for several hours to effect complete removal of the moisture. Care must be taken to avoid the use of a dehydrating agent which is soluble in, or has a chemical action upon, the liquid to be dried. For example, basic liquids like aniline must not be dried with acid agents such as phosphorus pentoxide, nor yet with calcium or zinc chlorides, which also unite with bases; on the other hand, caustic potash or lime, in small lumps, may be used. For ethereal salts, substances of neutral reaction, such as anhydrous sodium sulphate, are best.

The dried liquid should always be removed from the dehydrating agent before distilling. This is especially true when the agent is an anhydrous salt like sodium sulphate or calcium chloride, the hydration of which in the drying process is easily reversed by heat. Even when the substance is contained in a volatile solvent that may have been used for extraction from aqueous solution (51), the drying agent should be separated by decantation or filtration through dry paper, and washed with a little of the dry solvent.

GOVT. GIRLS COLLEGE
SUKKUR
844
LIBRARY

SECTION I

PHYSICAL MEASUREMENTS AND LAWS

24. The advances which have been made in the application of physical science to chemical problems, especially during the last quarter of a century, are so many and so varied, that the methods of teaching chemistry, and the whole approach to the science, have been profoundly changed. Certain aspects of physical chemistry have acquired such immediate and fundamental importance for a real understanding of chemical reactions and processes, that it seems desirable to introduce a brief account of them here. Those experimental laws, therefore, and the relevant theoretical matter, which are of the greatest interest to the beginner in the study of chemistry, have been discussed briefly in this section, more particularly in their bearing on the various branches of practical work. For a full treatment of such matters reference must be made to one of the many excellent books on physical chemistry, a subject which now forms an essential part of all chemical training.

Apart from the more theoretical foundations of the subject, there are certain laboratory methods for the determination of physical constants, such as boiling point and density, so important for the purification and identification of substances that every student should be familiar with them. These are accordingly placed first.

PHYSICAL MEASUREMENTS

25. **Determination of melting point.** The melting point of a substance is that constant temperature at which the solid passes into the liquid form. This temperature is most accurately determined by using a large quantity (at least 20 g.) of the material,

the vessel containing it being heated in a bath the temperature of which is a few degrees higher than that of the melting point required.

For ordinary laboratory purposes the melting point may be found with a sufficient degree of accuracy by placing some of the powdered substance in the closed end of a thin-walled capillary tube, made by drawing out a test-tube to a diameter of 1·5–2 mm. This small tube is then placed alongside of an accurate thermometer, and kept in position by a ring of rubber, cut from narrow rubber tube, and the two together are immersed in a small beaker

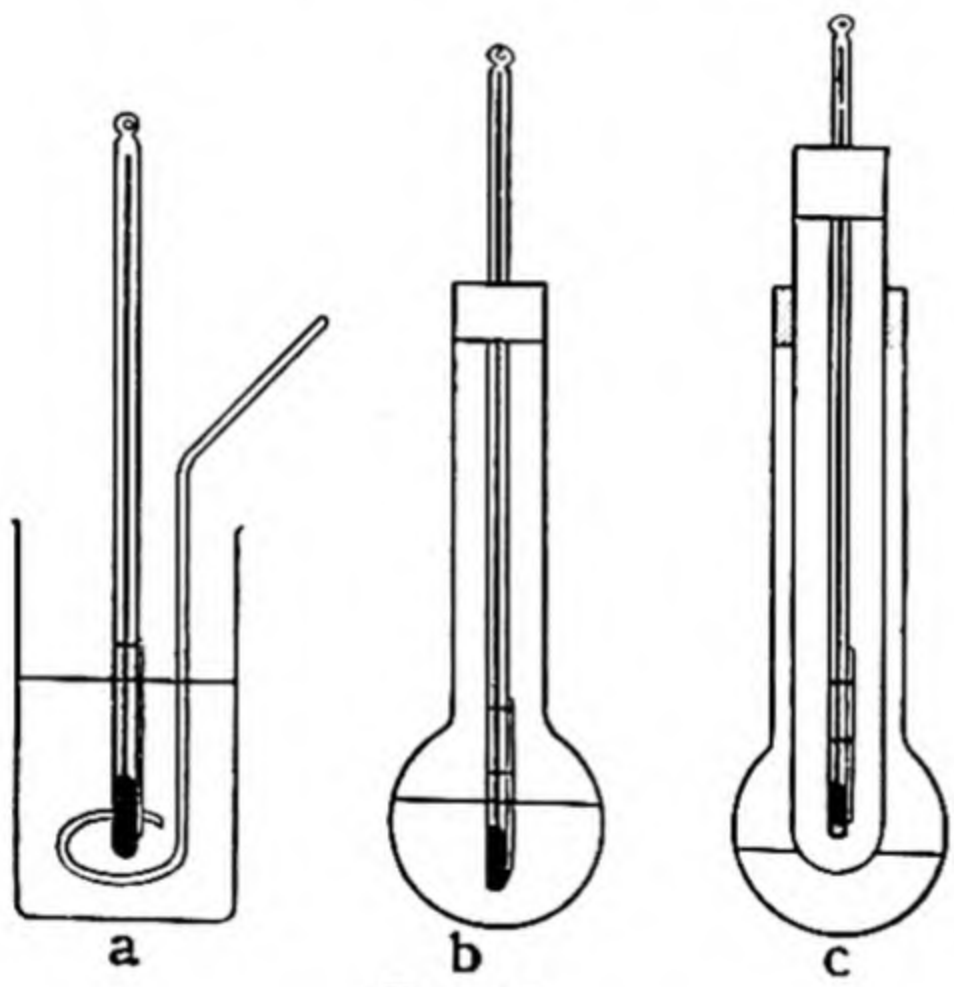


FIG. 30.

or tube of sulphuric acid or glycerol (Fig. 30, *a*). The ring of rubber may even be dispensed with, and the surface tension of the liquid will keep the two tubes in contact. The bath should be stirred by means of a glass stirrer, and very slowly heated over a small flame.

Instead of a beaker, a long wide-necked glass bulb (Fig. 30, *b*) may be used ; and the stirring dispensed with. To secure more uniform heating, the thermometer with capillary may be placed in a test-tube, which in turn is placed in the acid, which should just touch the bottom of the test-tube (Graebe, Fig. 30, *c*).

The temperature at which melting begins is the true melting point. This is constant for a pure substance, but is almost always considerably lowered by the presence of impurities.

For the purpose of identifying a substance with a known body, place three capillary tubes in contact with the thermometer, containing respectively the known substance, the unknown, and an intimate mixture of the two. If identical, all three will melt together, even on reheating. If not, the mixture will melt at a lower temperature, in general, than either of the others.

26. Determination of boiling point. The boiling point of a substance is that temperature at which the vapour pressure of

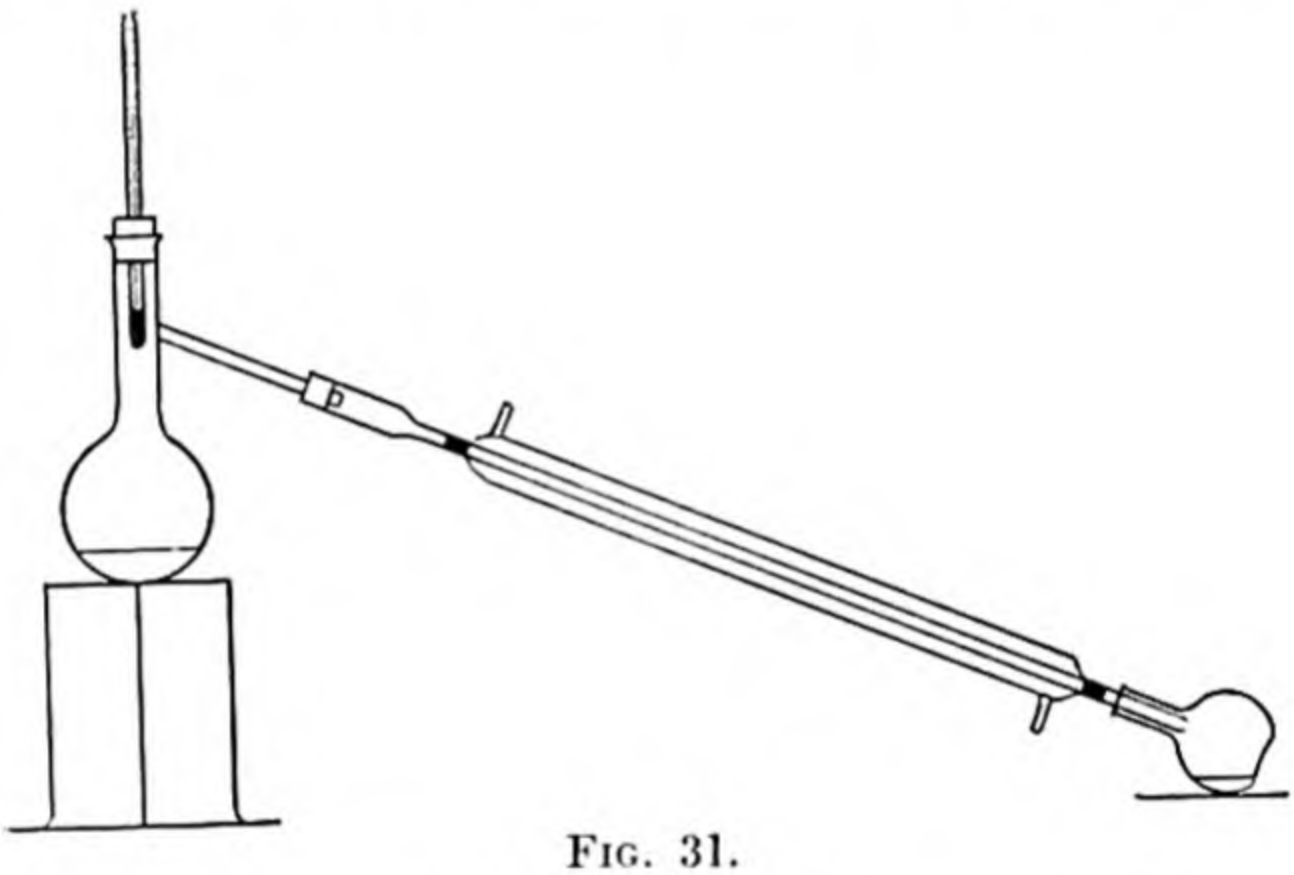


FIG. 31.

the substance is equal to the external pressure upon it. For a pure substance this temperature is constant at any specified pressure, and is raised by an increase of the pressure.

When at least 10–20 c.c. of the liquid are available, the usual method of determining the boiling point is to distil in a small distilling flask, heated by a small flame in contact with the bottom of the flask. To ensure regular boiling, some small pieces of porous clay, or clippings of platinum foil, should be placed in the liquid. The temperature is indicated by a thermometer inserted in the neck, with the bulb just below the side tube of the flask. The bulb thus becomes coated with a film of the pure liquid in contact with its saturated vapour, and the true boiling

point is found. Boiling, however, must be sufficiently rapid to keep the bulb entirely covered with vapour. Short range thermometers, the whole mercury column of which can be immersed in the vapour, are to be preferred. No correction for the emergent column of mercury is then necessary.

FIG. 32.

Correction of observed boiling point. If the mercury column emerges from the flask, which is generally the case if an ordinary long-range thermometer is employed, this mercury is at a lower temperature than that in the bulb, and the indication of the thermometer is too low. A correction must therefore be made. This is obtained by finding the mean temperature (t) of the emergent column, by means of a small thermometer lashed to the large one (Fig. 32), so that its bulb is half way up the emergent column.

Then $$\text{Correction} = 0{\cdot}000153\,(T - t)\,N^\circ \text{ C.},$$

where T is the observed boiling point, t the mean temperature of the cooled column, and N the number of degrees in the cooled column.

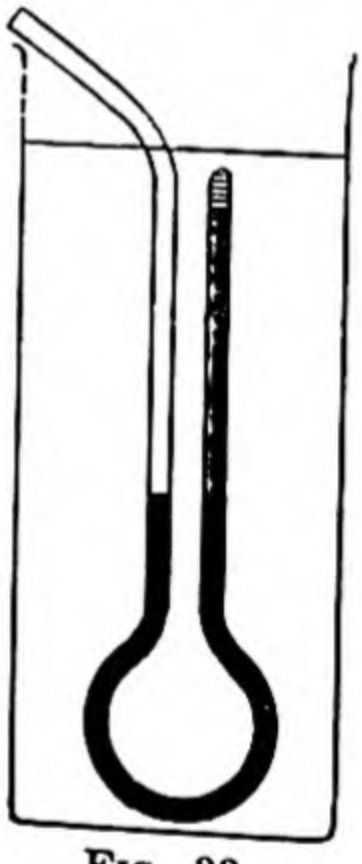


FIG. 33.

To obtain the boiling point under standard pressure the necessary correction is given by the expression

$$dt = \frac{T \,.\, dp}{9120},$$

where T is the observed boiling point on the absolute scale, and dp the difference between the observed and standard pressures.

27. When the quantity of liquid available is too small to allow of a boiling-point determination by the above method, others may be used. In the method of Chapman Jones * a bent tube (Fig. 33) contains a small quantity of the liquid, which is conveyed to the closed end of the inverted tube, and the open end is then placed under mercury in a small dish. The

* *J.C.S.* 1878, 175.

whole is now introduced in this position into the bath, which is then heated to the boiling point of the liquid. The vapour of the liquid expels all the air, and on cooling, mercury enters the tube. If any air bubbles remain, the operation is repeated. The tube is then carefully removed, the liquid made to occupy the closed end, and some mercury ejected until the mercury level is lower in the open than in the closed limb. The tube is then heated slowly in the bath, in the position shown, until the mercury stands at the same level in both limbs. Since the vapour pressure of the liquid must now equal the atmospheric pressure, the temperature of the bath is the boiling point of the liquid. Several observations should be made, with both rising and falling temperature. The quantity of liquid used must be sufficient to leave some unvaporised, that is, the vapour must be saturated.

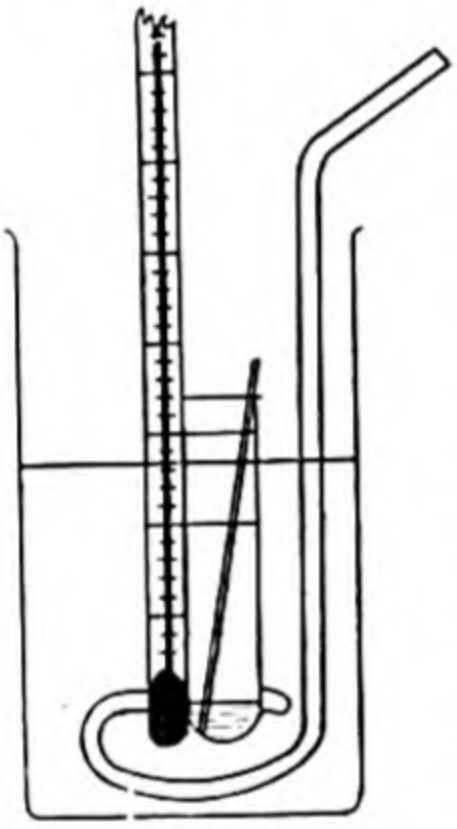


FIG. 34.

28. The method of Siwoloboff * gives the approximate boiling point with even one drop of the liquid. A narrow glass tube (Fig. 34) is sealed at one end, the liquid introduced, and a capillary tube, sealed about 1 cm. from the lower end, is placed in it. The tube is then fastened to a thermometer, so that the bulb is at the level of the liquid, and heated in a bath. Air bubbles escape from the lower end of the capillary, and these become more numerous as the temperature rises. When the boiling point is reached, a rapid stream of small bubbles of vapour is emitted from the liquid. Several observations should be made, each with a fresh capillary, and the average value taken.

29. **Determination of specific gravity.** For the determination of this constant, some form of pyknometer or specific gravity tube is required. The ordinary specific gravity bottle with perforated stopper may be used, but for accurate work a more exact instrument should be employed.

A convenient form is that shown in Fig. 35. It consists of a

* *Berichte*, **19**, 795 (1886).

glass tube, with narrow neck made from thermometer tubing, and a ground-in stopper. The neck has one or more marks etched round it. To use the instrument, it is filled with distilled water, suspended by a platinum wire in a beaker of finely crushed ice and water so as to give a temperature of 0° C., and left for an hour. The water level is then adjusted to one of the marks by means of a fine capillary, the tube removed, carefully dried and allowed to stand in the balance room for half an hour before weighing. Deducting the weight of the empty tube, the weight of the water is found. The dry tube is now filled with the liquid to be examined, placed in the bath for an hour, the volume adjusted as before and the whole weighed. It is customary to determine the constant also at another temperature, 15° or 20°. The tube, after filling with the liquid, is placed in a bath at the required temperature, the liquid adjusted as before and weighed.

FIG. 35.

Another form of pyknometer very commonly used is Perkin's modification (Fig. 36) of the Sprengel tube. This consists of a U-tube, the ends of the two limbs being connected to capillary tubes which are bent at 135° with them, and which are therefore at right angles to each other. On one of the capillaries is a small bulb, and a mark is etched between this and the upper end of the limb. The ends of the capillaries are furnished with ground-on caps. The instrument is filled by dipping the plain capillary in the liquid, and applying suction at the other, until the bulb is half filled. It is then placed in the ice bath, and after an hour (with caps on) the volume is adjusted by removing the caps and tilting the tube so that the plain capillary is horizontal, the other being vertical, and withdrawing liquid by means of filter paper

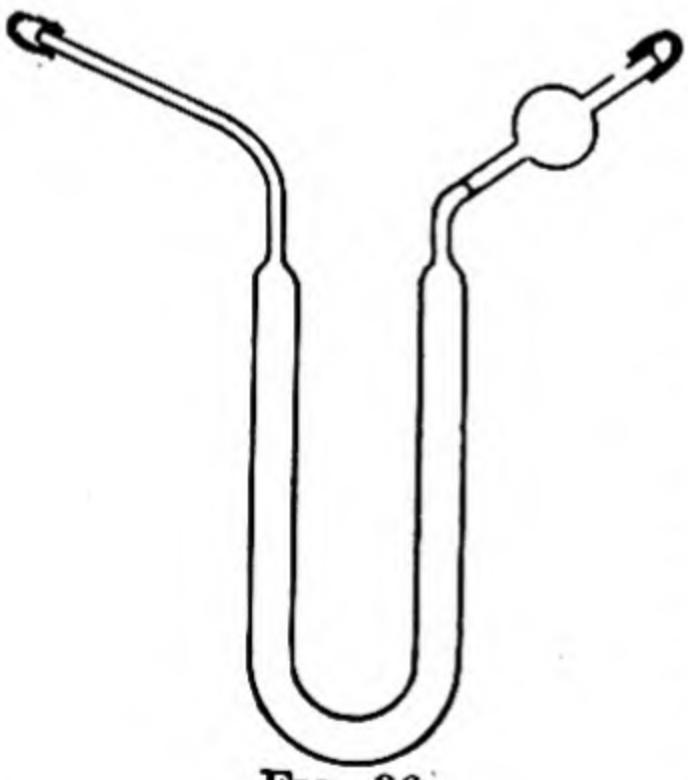


FIG. 36.

placed in contact with the end of the capillary, until the liquid in the bulbed capillary has fallen exactly to the mark. The caps are then replaced, and the tube carefully dried, and weighed after standing in the balance room for half an hour.

From the weight of water at 0°, the weight at 4° should be calculated, and the density referred to this. For example, for alcohol

$$D^0/_4 = 0{\cdot}806\ ;\ D^{20}/_4 = 0{\cdot}789.$$

30. Determination of molecular weight. The empirical formula obtained from the analysis of a substance may not represent the true molecular magnitude, which may be a multiple of the simplest formula. The true molecular weight must therefore be determined by an independent method, of which there are several. For volatile liquids, and solid substances which may be readily vaporised without decomposition, a convenient method is to find the vapour density.

Vapour density. An accurate determination of this may be made by Dumas' method of vaporising the substance in a globe or bulb of known volume, which is then sealed and weighed when cold. For the purpose of molecular weight determination, however, great accuracy is not usually required, since it is necessary only to decide between the empirical formula and a multiple of it. The method commonly used is one devised by Victor Meyer, which is rapid and gives results correct to within five per cent.

A long glass tube (*A*, Fig. 37) ending in a cylindrical bulb of 100–200 c.c. capacity is furnished near the top with a capillary delivery tube, and a short side tube through which a glass rod moves in a rubber fastener. The long tube is supported in a wider tube *B*, containing a liquid whose vapour when boiled heats the bulb *A*. The boiling point of this liquid should be at least 30° above that of the substance to be examined. The bottom of *A* is covered with dry sand or asbestos wool to break the fall of the small tube containing the substance, and the bath is then heated until the air in *A* has expanded so that no more escapes from the delivery tube. Meanwhile the substance is weighed in a small stoppered tube, and placed in the upper end of *A*, resting on the end of the glass rod. *A* is then closed. When

all is ready, and no more air bubbles escape from the delivery tube, the glass rod is withdrawn to allow the substance to drop, and at once replaced. Vaporisation takes place rapidly, and the expelled air is collected in the graduated tube. The intention is that the vapour should be produced quickly, and being heavier than air, should lift the air without any appreciable diffusion. If this occupies too much time, diffusion of vapour into the upper part of the tube, where it may be condensed, will affect the result. When no more air is expelled, the graduated tube is removed to a tall cylinder filled with water in which it is immersed for 15 minutes. The temperature, and the volume at atmospheric pressure, are then observed.

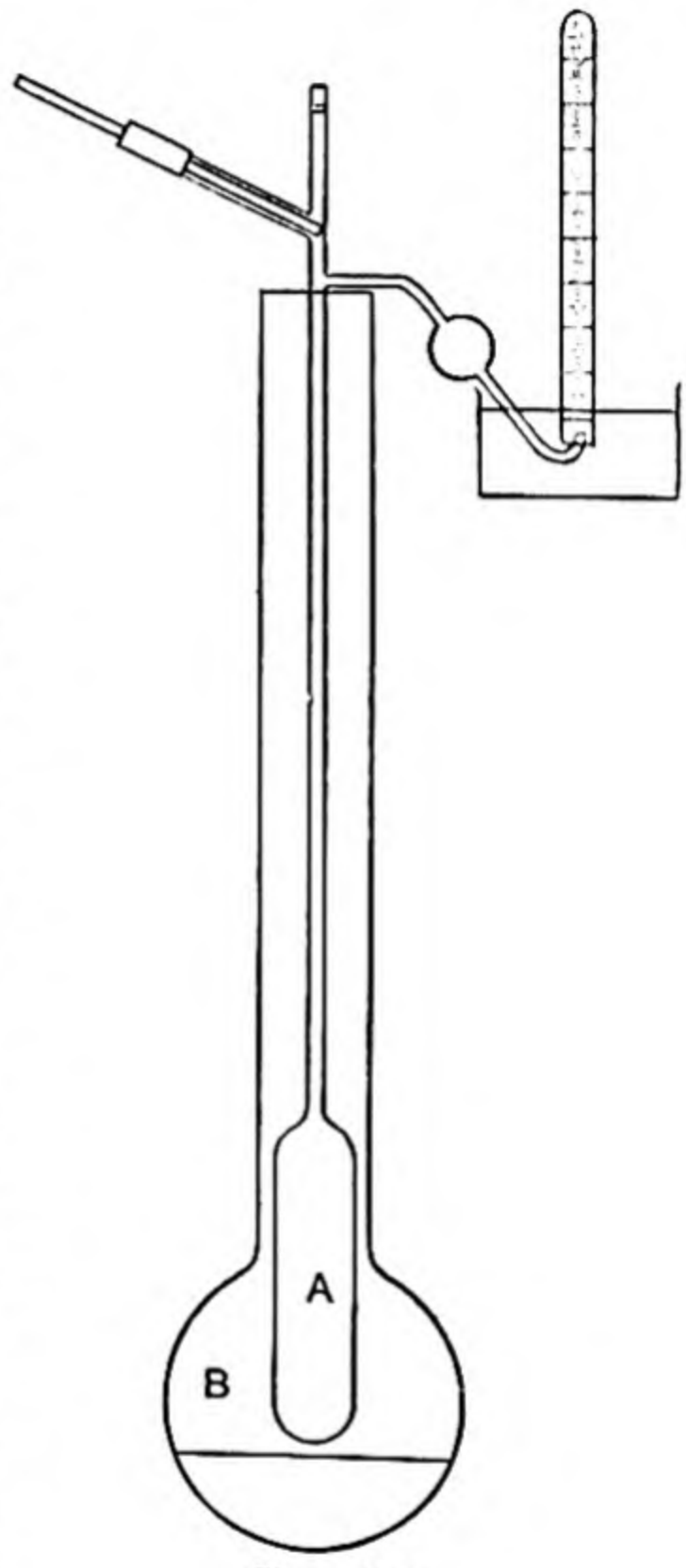


FIG. 37.

This volume is the volume which would be occupied by the vapour of the substance if it could exist as vapour at the temperature and pressure of the air in the graduated tube. The fact that the vapour in A is produced at the much higher temperature of the bath, and that there is a falling temperature gradient between the bath and the collecting tube, has no influence on the result. The only requirement is that the experiment should be conducted rapidly in order to avoid diffusion and loss of vapour.

The vapour density is now calculated as follows :

Let W = weight of substance used,
,, V = volume of air collected,
,, t = temperature of this air,

Let p = barometric pressure,
,, a = vapour pressure of water at $t°$.

Then the vapour density of the substance referred to that of oxygen as 16 is given by the formula :

$$D = 16\,\frac{W}{V}\cdot\frac{760(273+t)}{(p-a)\times 273\times 0{\cdot}001429}.$$

The molecular weight referred to that of oxygen as 32 is twice the vapour density.

Other methods of determining molecular weights are described in the section on solutions (59).

31. Molecular weights of organic acids. The sodium and potassium salts of the simple organic acids are destroyed by ignition, leaving the carbonate of the metal. From the weight of this, the molecular weight of the acid may be deduced, but in many cases the carbon set free during the ignition is difficult to burn away completely. It is better to use the silver salt, which leaves a residue of metallic silver. A weighed quantity (W) of the dry salt is heated in a weighed porcelain or silica crucible, at first gently, then more strongly, and finally over the blowpipe until the weight is constant. The residue (R) is pure metal. The loss in weight represents the radical of the acid, so that the ratio

$$\frac{W}{R} = \frac{107{\cdot}88 + E - 1}{107{\cdot}88},$$

and the equivalent weight of the acid is therefore

$$E = \frac{107{\cdot}88(W-R)}{R} + 1.$$

If the equivalent weight is multiplied by the basicity of the acid, the molecular weight will be found.

For the sulphate method of determining the molecular weights of organic or volatile acids, see par. **520**.

For the determination of Equivalents, see par. **414**.

32. Molecular weights of organic bases. Organic bases in the form of their hydrochlorides form double salts with platinic and auric chlorides, of the same type as those formed by ammonium chloride. They are usually well crystallised compounds of the

composition $(B\ .\ HCl)_2PtCl_4$ and $B\ .\ HCl\ .\ AuCl_3$ respectively, and are readily prepared by adding platinic chloride or gold chloride solution to a concentrated solution of the hydrochloride of the base. The salts are usually sparingly soluble in water, less soluble in alcohol, and are therefore easily purified. When heated these double salts are decomposed, leaving a residue of the pure metal. As in the previous experiment, therefore, about half a gram of the dry salt (W) is accurately weighed into a weighed crucible, and carefully heated, finally over the blowpipe until the weight of the residue (R) is constant. In the case of a platinichloride of the above formula, we have

$$\frac{W}{R} = \frac{(B\ .\ HCl)_2PtCl_4}{Pt} = \frac{2B + 2HCl + Pt + 4Cl}{195{\cdot}23},$$

from which the equivalent (B) of the base is

$$B = 97{\cdot}615\,\frac{W}{R} - 204{\cdot}965.$$

In the case of aurichlorides a similar method of calculation is used in accordance with the composition of the salt.

SOME PHYSICAL LAWS

33. The behaviour of gases. Changes of temperature and pressure cause well known and very simple changes in the volume of a gas. Since under these changing conditions all gases, and all mixtures of gases in which no chemical reaction occurs among the constituents, behave in the same way, the idea was long ago conceived that all gases are similarly constituted. The suggestion that a gas is composed of separate moving particles was first made by Robert Hooke in 1678, and used by Daniel Bernoulli in 1738. Joule calculated the mean velocity of those particles in 1851, and by the later work of Clausius and Clerk-Maxwell the modern kinetic theory of gases was firmly established.

34. The kinetic theory. The theory of moving particles at once explains the expansive property of gases, by virtue of which

a gas fills the whole of the space containing it. And if various gases be admitted into the same space, they mingle with each other, or diffuse into each other, until the composition of the mixture is everywhere the same. Consequently in any given volume of this space there is on the average the same number of molecules ; in other words, the density is the same at all points, and the density of any one constituent is also uniform.

Each molecule is in frequent collision with other molecules, from which, the elasticity being perfect, it rebounds with altered direction and velocity, but without change in the total energy. All molecules thus have not the same velocity, but we may consider that there is an average velocity of the molecules, which increases with increase of temperature.

35. **Boyle's law.** The impacts of the particles affect not only other particles, but also the walls of the containing vessel, upon which they produce the effect we call pressure. Let this pressure be represented by p, the volume by v, and let the mass of a particle be m, the number of such particles n, and the average velocity of the particles c. Then it may easily be shown that

$$pv = \tfrac{1}{3}mnc^2.$$

This may be written $\frac{2}{3} \cdot \frac{1}{2}mnc^2$. But $\frac{1}{2}mnc^2$ is the total kinetic energy of the gas, so that the product of the pressure and volume of a gas is equal to two-thirds of the kinetic energy of its molecules. Since the kinetic energy is constant at constant temperature, the product pv is also constant. This is Boyle's Law.

36. **Charles' law.** It is clear that equal volumes of different gases under the same conditions must have the same total kinetic energy, and this is true for all values of the kinetic energy, which, for all gases, is proportional to the absolute temperature. The increase of pv with temperature is therefore due to the increase in the total kinetic energy of the gas molecules, and must be the same for all gases. At constant pressure, therefore, the volume of a given mass of gas is proportional to the absolute temperature. This generalisation is known experimentally as Charles' Law.

37. The general gas equation. It follows that pv/T is constant for a given mass of gas, or $pv = rT$, where r is a constant. The numerical value of r will depend upon the mass of the gas and upon the units in which p and v are expressed. Since the gram-molecular volume is the same for all gases, under the same pressure, we may generalise the gas equation by using this value, and the expression PV/T is the same for all gases, where P and V represent the pressure and volume respectively of one gram-molecule. We then have the general equation for an ideal gas :

$$PV = RT, \text{ or } \frac{PV}{T} = R,$$

in which R represents the work done per unit rise of temperature by one gram-molecule of the gas expanding against a pressure P. The value of R in litre-atmospheres at normal temperature and pressure is then

$$R = \frac{PV}{T} = \frac{1 \times 22{\cdot}412}{273{\cdot}2} = 0{\cdot}08203,$$

or, using approximate values,

$$R = \frac{1 \times 22{\cdot}4}{273} = 0{\cdot}0821 \text{ litre-atmospheres.}$$

Since all gases deviate from Boyle's law to some extent, the gram-molecular volume is not quite constant, and the value of R derived from it is therefore not quite the same for all gases. The value 22·412 used above is the average of the values found for hydrogen, oxygen and nitrogen.

The approximate constancy of the gram-molecular volume of gases may be illustrated in the following simple manner. One gram of marble, which contains $\frac{1}{100}$ of a gram-molecule of CO_2, is dissolved in dilute HCl, and the liberated gas collected over saturated salt solution, in order to minimise loss. The volume is measured. The apparatus used for determining equivalents may be employed. Similarly, 0·65 g. of zinc, which displaces $\frac{1}{100}$ of a gram-molecule of hydrogen, is dissolved. The two gas volumes will be practically equal.

The molecular weight of a gas may be determined approxi-

mately by multiplying the gram-molecular volume by the density, that is, the weight in grams of one litre at N.T.P.

The gas constant R has the dimensions of work or energy, and may therefore be expressed in terms of different energy units. To convert it into thermal units it must be divided by the mechanical equivalent of heat, $J = 42{,}350$. We thus have

$$R = \frac{PV}{T} = \frac{1033 \times 22{,}400}{273 \times 42{,}350} = \frac{84{,}759}{42{,}350} = 2.$$

R is therefore approximately equal to 2 calories, and with this value the general gas equation for molecular quantities becomes

$$PV = 2T.$$

In this form the gas equation may be used to calculate the thermal equivalent of the work done upon or by a gas when it changes its volume under changes of external pressure. If a gram-molecule of a gas is liberated, for example, by such reactions as those cited above, the work done by the gas in expanding against the external pressure of one atmosphere will involve the absorption of a quantity of heat equal to $2T$ calories, or 546 calories if the reactions occur at 0°. Further reference to this equation will be made in discussing the laws of dilute solutions (57, 58).

38. Avogadro's law, that under the same conditions of temperature and pressure equal volumes of gases contain equal numbers of molecules, may be deduced also from the kinetic theory. For, let two gases have equal values of the pressure and volume, so that $p_1 v_1 = p_2 v_2$; then

$$\tfrac{2}{3} m_1 n_1 \frac{{c_1}^2}{2} = \tfrac{2}{3} m_2 n_2 \frac{{c_2}^2}{2},$$

but the average kinetic energy of a molecule is the same for both gases, since the temperatures are equal, so that :

$$\frac{m_1 {c_1}^2}{2} = \frac{m_2 {c_2}^2}{2};$$

$$\therefore \; n_1 = n_2 ;$$

that is, the number of molecules per unit volume is the same for both gases.

This generalisation, like the pressure-volume law of Boyle, and the temperature-volume law of Charles, applies to all gases within certain limits, namely under conditions of temperature and pressure remote from those pertaining on the one hand to the liquid state, or on the other to the dissociation of the gas molecules. All three laws apply, with corresponding reservations, to dilute solutions, the pressure in this case being the osmotic pressure of the solution.

39. Gaseous diffusion. The velocity of a molecule may be expressed, from the equation $pv = \frac{1}{3}mnc^2$, as

$$c = \sqrt{\frac{3pv}{mn}};$$

and since mn is the total mass of the gas, $\frac{v}{mn}$ is the reciprocal of the density; thus

$$c = \sqrt{\frac{3p}{d}}.$$

Hence the speed of the molecules of a gas is inversely proportional to the square root of the density. Although the actual velocities cannot be directly measured, this relationship is an expression of the experimental law of the diffusion of gases discovered by Graham in 1861.

The actual average speed of the molecules may be calculated by inserting the requisite values in the above expression. For oxygen at normal temperature and pressure, the volume of one gram is $\frac{1}{0{\cdot}00143}$ or 699·3 c.c., the pressure in dynes per sq. cm. is $13{\cdot}60 \times 76 \times 981$, so that

$$c = \sqrt{3 \times 13{\cdot}60 \times 76 \times 981 \times 699{\cdot}3}$$
$$= 46{,}120 \text{ cm. per second},$$

or the molecule of oxygen moves under normal conditions at about 18 miles per minute.

The objection has been raised to the kinetic theory that in spite of these large velocities, a gas set free at one point in a large room is perceptible at a distant point, say by smell, only after the

lapse of some time. Clausius pointed out, however, that the progress of any one particle is impeded by its collisions with others, and its direction of motion also is constantly changed. The free path of a molecule is very short, and its actual path is a maze of short straight lines.

40. Kinetic theory of a compressed gas. When gases are strongly compressed, certain deviations from Boyle's law are observed. The actual volume of the molecules themselves, which at ordinary pressures is negligible in comparison to the total volume, becomes an appreciable fraction of the much smaller volume occupied by the gas at high pressures. The effective volume in which the molecules move is no longer v, but $(v-b)$, where b is a constant for each gas depending on the size of the molecules of the gas. It is taken on different views as either four times or $4\sqrt{2}$ times the actual volume of the molecules. Instead of the equation $pv = RT$, we have therefore

$$p(v-b) = RT.$$

In addition to this, another factor becomes effective at moderately high pressures, namely, the attractive forces between the molecules which cause cohesion in the liquid and solid states. This attractive force has the effect of an added pressure, which van der Waals (1879) assumed to be proportional to the inverse square of the volume. The pressure is therefore increased by the factor $\frac{a}{v^2}$, a being a constant depending on the nature of the substance. Van der Waals' equation therefore becomes

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = RT.$$

The great majority of gases exhibit such deviation from the ideal law of Boyle, the product of pressure and volume at first decreasing slightly as b becomes operative, and afterwards increasing with increasing pressure as a becomes more important. The deviations from the ideal law are less at higher temperatures, although the constants a and b are independent of the temperature.

41. Kinetic theory of liquids. Van der Waals' equation is applicable not only to compressed gases, but to the critical condition of a substance and the passage of a gas into the liquid state. The molecules of a liquid are much closer together than are those of the same substance in the form of gas or vapour, and their movements are consequently much more restricted; but they are nevertheless in continual motion, constantly passing from the liquid phase to the vapour phase and *vice versa*. If we have a vessel containing a liquid *A* (Fig. 38), and all other matter be excluded from the vessel, molecules of the liquid will pass into the space above the liquid until the pressure p of the vapour attains a maximum limiting value which increases with the temperature. This maximum pressure is called the vapour pressure of the substance. If the volume be now increased, the temperature being kept constant, more vapour is formed so that the maximum value p of the pressure is maintained, and ultimately all the liquid is converted into vapour. Any further increase of volume now causes a decrease of the pressure in accordance with Boyle's law. On the other hand, if the volume be diminished, since the pressure p cannot increase, some vapour condenses until with continued decrease of volume it all assumes the liquid form. If the liquid, instead of being enclosed as above suggested, is contained in an open vessel, the molecules of vapour diffuse into the atmosphere in accordance with Graham's law, and the liquid evaporates more or less rapidly.

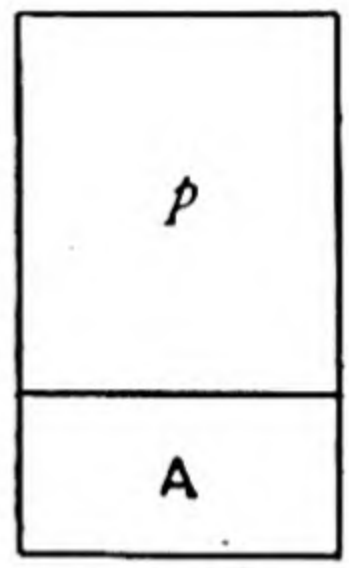


FIG. 38.

All such phenomena are explained by the application of the kinetic theory to liquids, and take place very closely in accordance with the corrected equation of van der Waals.

SOLUTIONS

42. Mixtures of gases may be regarded as solutions of one gas in another, a solution being definable as any stable homogeneous mixture of two substances. The solution of a gas in a liquid is

analogous to the condensation of a vapour in its own liquid. Molecules of the gas come into contact with the liquid, and some of them enter, that is, become dissolved and diffuse into the liquid, again leaving it if they chance to reach the surface with sufficient momentum. This continues until, as the concentration of the gas in the liquid increases, the numbers of gas molecules entering or leaving the liquid in unit time are equal. There is then a balance or equilibrium between the gas and its solution, the latter being saturated. Since the number of gas molecules striking unit area of the liquid surface in a given time is proportional to the pressure, the solubility of the gas is also proportional to the pressure, or

$$C = kP,$$

k being a constant. This is **Henry's law** (1805). The temperature of course is supposed to be constant. All gases become less soluble with increase of temperature; in other words, the solubility coefficient (S) or the volume of the gas that can dissolve in one volume of the liquid, diminishes with rise of temperature.

In a mixture of gases, each gas behaves as though the others were not there, and Dalton in 1807 found that each gas dissolves according to its own final partial pressure in the mixture. Each gas has also its own solubility coefficient. Consequently the composition of a gas mixture is changed by solution in a liquid, as in the well-known case of dissolved air.

It should be added that the molecular magnitude of a gas obeying Henry's law must be the same in the gas phase and in solution: hydrate formation may occur, but without change in the size of the gas molecule. All the common gases obey Henry's law in aqueous and many in alcoholic solution, and acetylene also in acetone. If the molecular mass is not the same in the gas and solution phases, the absorption law is changed. If, for example, a gas dissolves in the form of double molecules, the concentration in the liquid is

$$C = kP^2.$$

The formation of hydrates, however, or in general, union with molecules of the solvent, has no influence on the law of absorption.

The laws of Henry and Dalton are fulfilled most perfectly for gases that are not very soluble, and at comparatively low pressures. But even when at ordinary temperatures the solubility of the gas is large and involves a chemical action with the solvent, this may disappear at higher temperatures. Thus sulphur dioxide dissolves in water in accordance with Henry's law above 50°, and ammonia above 100°. The *ionisation* of hydrogen chloride (75) in solution explains its entire departure from Henry's law.

43. Mixed liquids may be classified as completely miscible, like alcohol and water, and partially miscible, like water and ether, although this is only a qualitative distinction. The physical properties of mixtures are not, as a rule, those calculated in accordance with the proportions of their constituents, and form a very interesting study. The vapour pressures are especially important in regard to the separation of such mixtures by distillation. This will be considered later (47).

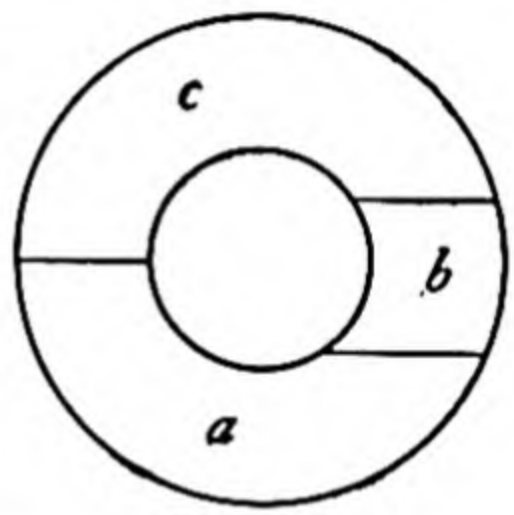


FIG. 39.

Partial miscibility may be regarded as the mutual solubility of liquids in one another. When ether, for example, is shaken with about an equal volume of water the two liquids separate again on standing, but each is now saturated with the other. At the ordinary temperature the water now contains about 3 per cent. of ether by volume, and the ether about 10 per cent. of water. The two layers, or phases, have necessarily the same vapour pressure, or no equilibrium could be established. In the diagram (Fig. 39), in which *a* represents water, *b* ether, and *c* the vapour phase, say in a circular tube or double cylinder, distillation would occur at the surface of higher vapour pressure, and condensation on that of lower vapour pressure. This is not possible without expenditure of energy. The equilibrium therefore involves not only a constant concentration of each liquid in the other, but a common vapour pressure, also constant at a given temperature.

Change of temperature always affects solubility. That of a

gas in a liquid decreases with increase of temperature. Volatile liquids in less volatile solvents approach the behaviour of gases, becoming as a rule less soluble as the temperature rises. When two liquids are partially miscible, and neither is volatile, it frequently happens that the solubility of each in the other increases with rising temperature. The two phases are called conjugate solutions. In such a case the solubility curves approach each other and meet at a point, called the consolute point, at and above which the two liquids are completely miscible. The diagram (Fig. 40) shows such curves for water and aniline, and for water and phenol. Some pairs of liquids have also a lower consolute temperature, and some have both, so that a closed curve is formed, as in the case of nicotine and water.

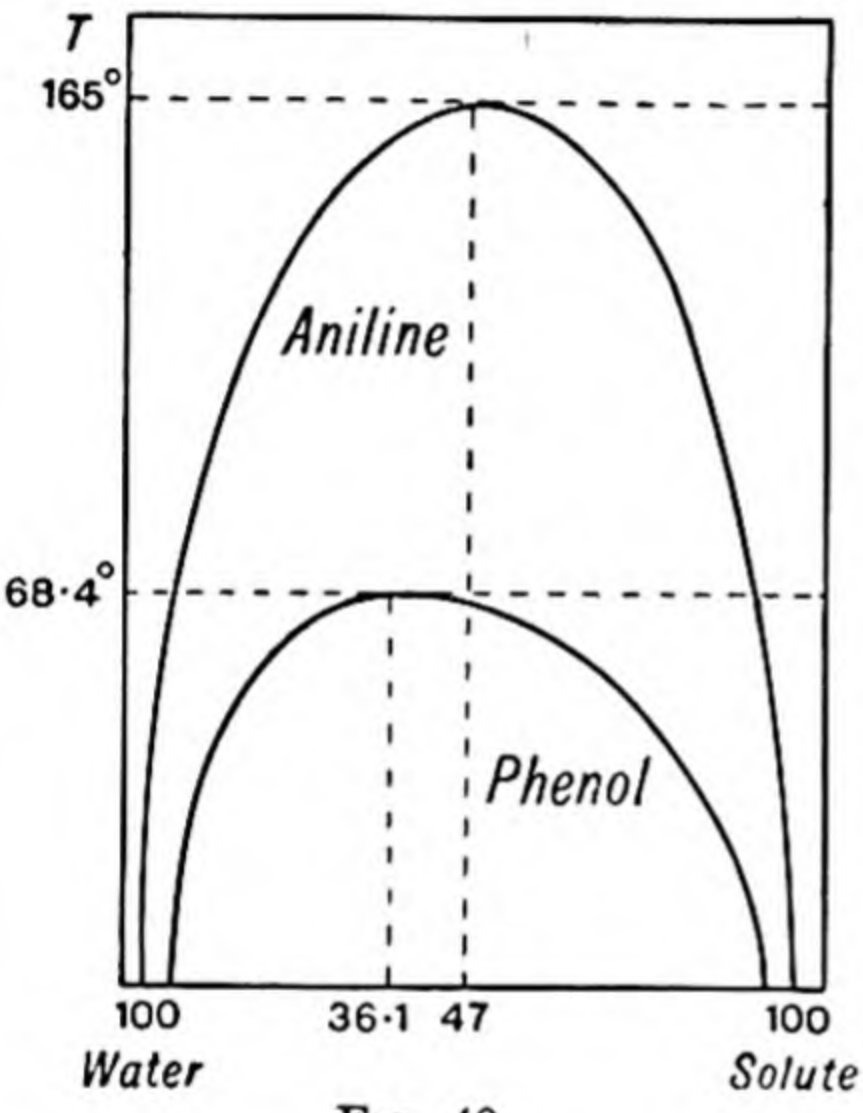


FIG. 40.

44. Distillation of mixed liquids. When a substance is dissolved in a liquid, the vapour pressure of the liquid is always lowered. In other words, the vapour pressure of a solution at a given temperature is always lower than that of the pure solvent.

Two perfectly **immiscible liquids** therefore present the ideal case in which neither liquid has any influence on the vapour pressure of the other. When such liquids are distilled together, they therefore pass over in a constant proportion depending on the ratio of the vapour pressures at the temperature at which the sum of these vapour pressures is equal to the atmospheric pressure, that is, at the boiling point of the mixture. The actual weights of the two liquids in the distillate are quite independent of the quantities in the original mixture. If C, p, and M represent

the molecular concentrations, vapour pressures and molecular weights of the two substances in the vapour, then

$$\frac{C_1}{C_2} = \frac{p_1 M_1}{p_2 M_2}.$$

The ratio C_1/C_2, and therefore the proportion of the two liquids in the distillate, remains constant until one of the liquids is completely distilled.

45. Steam distillation. The most important application of this principle is the process of steam distillation so often employed for the purification of organic substances when these are practically

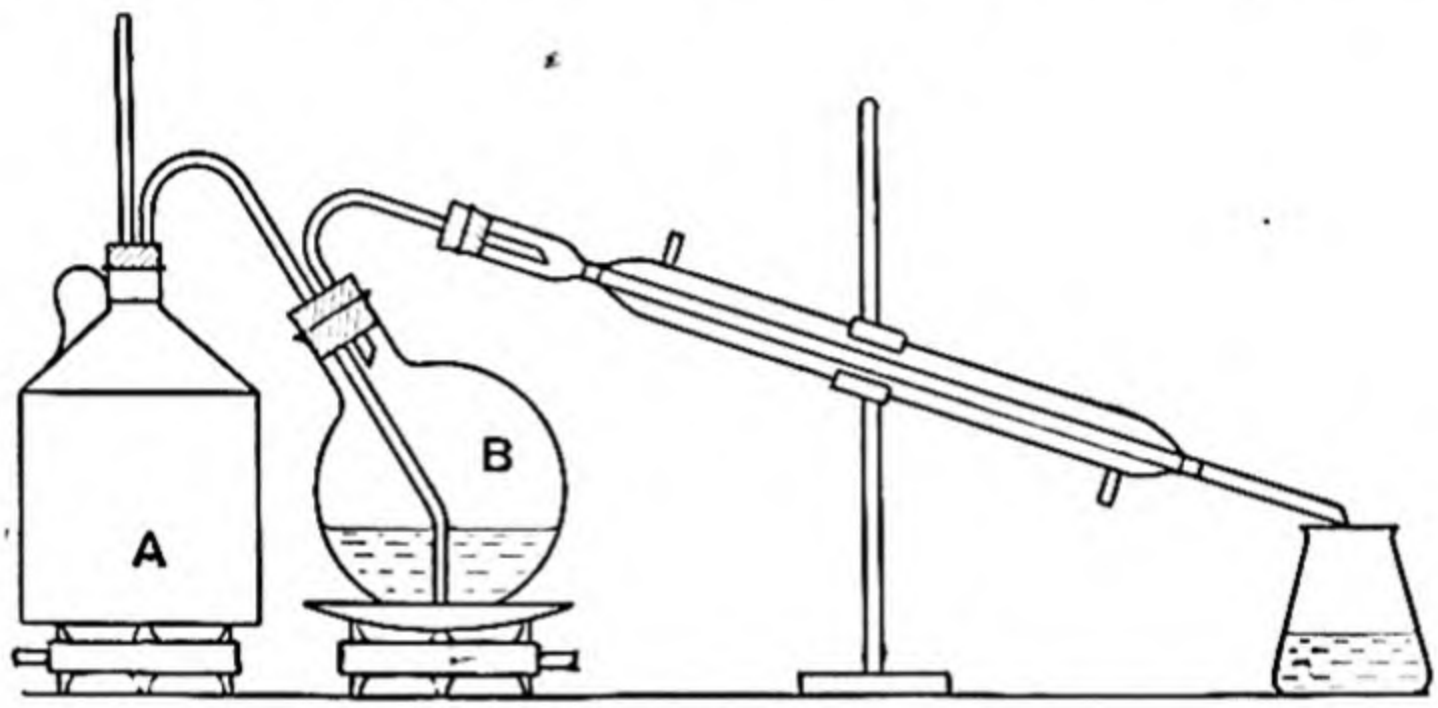


FIG. 41. Steam distillation.

insoluble in water. The metal boiler *A* (Fig. 41) is used for generating the steam, which is blown through the mixture of the substance with water in the flask *B*. This should be tilted as shown to reduce the risk of liquid being blown over into the condenser. *B* is kept warm by a flame sufficient to maintain its temperature, and so avoid the condensation of steam in the flask which would otherwise occur, and might increase the volume of liquid to an inconvenient amount.

The vapour pressure of the substance to be distilled is usually much less than that of water. The process may thus be regarded as a special case of distillation under reduced pressure (50). The molecular weight of the substance is, however, higher than that of water, and the proportion of substance in the distillate is there-

fore in most cases quite considerable. One or two examples will make this clear.

A mixture of nitrobenzene and water boils at 99·2° under the standard pressure of 760 mm. At this temperature water has a vapour pressure of 733 mm., and the partial pressure of nitrobenzene in the vapour is therefore 27 mm. The molecular weight of nitrobenzene is 123, that of water being 18, and the ratio of their weights in the distillate will be :

$$\frac{w_1}{w_2} = \frac{18 \times 733}{123 \times 27} = 3{\cdot}97.$$

In spite of the disparity in vapour pressures, the weight of nitrobenzene is thus about one-fifth of the total weight of liquid distilled.

Bromobenzene also is practically insoluble in water and the mixture distils at 95°. At this temperature the vapour pressure of water is 641 mm., that of bromobenzene 119 mm. The two liquids in the distillate are therefore in the ratio :

$$\frac{w_1}{w_2} = \frac{18 \times 641}{157 \times 119} = 0{\cdot}62,$$

and the bromobenzene in the distillate thus weighs more than one and a half times as much as the water.

For aniline (249) and *o*-nitrophenol (286) the boiling points of mixtures with water are respectively 98° and 99·4°, and the water ratios in the distillate 2·58 and 7·16. These numbers may all be confirmed by experiment.

46. Partially miscible liquids show a less simple behaviour. The common vapour pressure (43) of the two phases is somewhat less than the sum of the vapour pressures of the pure liquids, since each liquid has had its vapour pressure lowered by dissolving some of the other. On distillation, the two layers have the same boiling point, and the vapour distilled from each has the same composition, the distillate generally separating into two layers which are in a constant proportion until the substance present in smaller quantity has all passed over. These results

are in this case also quite independent of the relative amounts of the two liquids in the original mixture.

47. Completely miscible liquids are much more complex in their behaviour on distillation. The vapour pressure of the mixture usually bears no simple relationship to that of either of the pure liquids, and the composition of the vapour, and that of the mixture, are continually changing as the distillation proceeds.

Vapour pressure of mixtures. It seldom happens that the vapour pressure, and consequently the boiling point, of a mixture are strictly proportional to the composition, as indicated by the dotted line AB in Fig. 42, in which the vapour pressures are represented on the ordinates, the composition of the mixture on the abscissae :

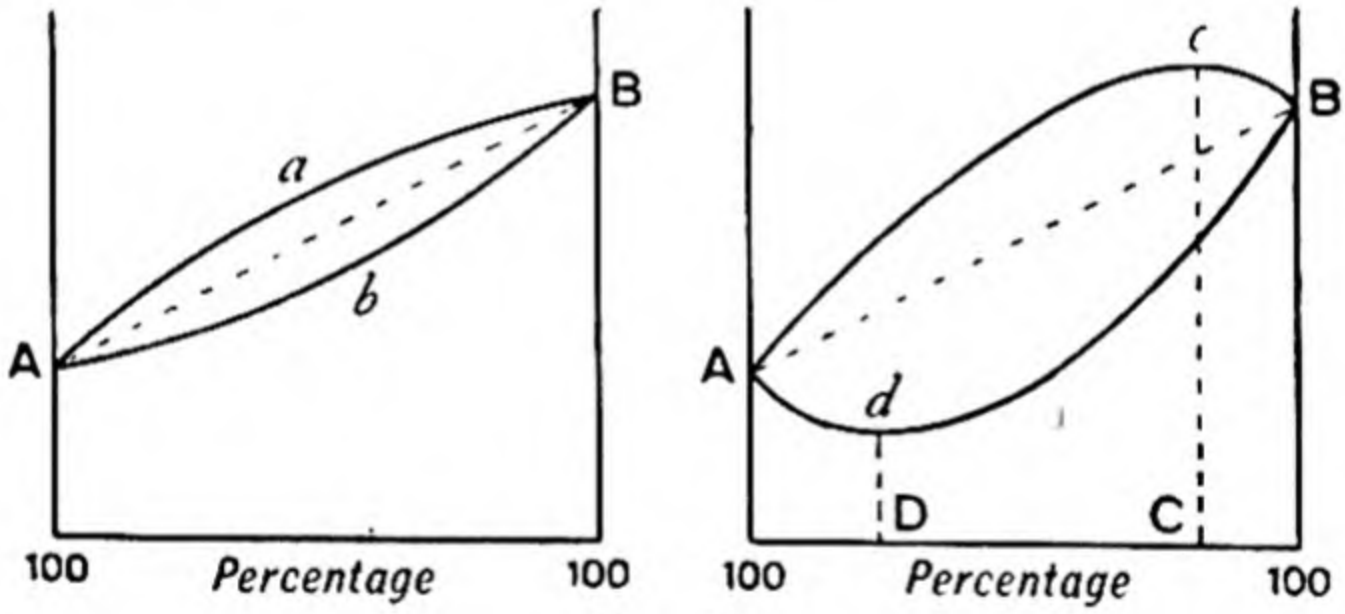


FIG. 42.

The more usual form of the vapour pressure curve for the mixture lies a little above the straight line, as AaB, or a little below it, as AbB. So long as no part of the curve lies below the vapour pressure of the less volatile liquid A, or above that of the more volatile liquid B, it is possible to separate the two liquids by distillation.

When the vapour pressure curve, on the other hand, rises to a maximum, as at c, or falls to a minimum, as at d, the pure liquids cannot be separated. On the contrary, a mixture showing the curve AcB will separate on distillation into the more volatile, lower boiling mixture C, called an azeotropic mixture, and one

of the less volatile constituents A or B, this depending on the original proportions of A and B. The mixture C, however, is of constant composition and constant boiling point, whatever the original proportions of A and B. An example of this is found with mixtures of alcohol and water, for which the maximum vapour pressure is given by alcohol containing 4·4 per cent. of water, boiling at 78·13°. The water cannot be separated from this by simple distillation.

Mixtures for which the vapour pressure composition curve shows a minimum value, as AdB, are comparatively rare, and are also incapable of being separated into the two pure liquids by distillation. They yield instead a mixture D of maximum boiling point, which remains when the excess of either A or B has been distilled. Such a mixture will therefore separate into one or other of the pure constituents, whichever is present in excess of the composition D, and the high-boiling mixture D, which is of constant boiling point and constant composition under any given pressure.

48. Fractional distillation. It is not to be expected that a mixture of completely miscible liquids, showing a continuous change of vapour pressure, will separate into its constituents of high and low boiling points, whether these be the pure liquids or constant boiling mixtures, as the result of a simple distillation. The separation of such liquids is effected by the process of fractional distillation, which is aided by the use of a fractionating column. In such columns obstruction is offered to the passage of the vapour, the less volatile constituents of which are condensed and returned to the flask. In passing down the column the condensed liquid meets the vapour coming from the flask, cools it and partially condenses it, while at the same time part of the more volatile constituent of the condensed liquid is vaporised. A considerable separation of the two liquids is thus effected in one distillation. Some laboratory still-heads or fractionating columns are illustrated in Fig. 43, a being a Glinsky form, and b and c Young and Thomas types. These are very efficient.

A more complete separation may be effected by collecting the

distillate in several fractions, at definite ranges of temperature, and redistilling them. When the first fraction is redistilled to the original temperature limit, there will be a residue of higher boiling substance. The second fraction is now added, and on distilling, some liquid will pass over in the first range, and be collected in the first fraction, while most will come in the second fraction, again leaving a residue at the second temperature limit. The third fraction is now added and the distillate collected in fractions as before, observing the same temperature ranges throughout. On a repetition of the process it will be found that the distillates accumulate near the boiling points of the constituents. The number of fractions chosen, and the number of repetitions, will depend on the nature of the liquids and the boiling point range.

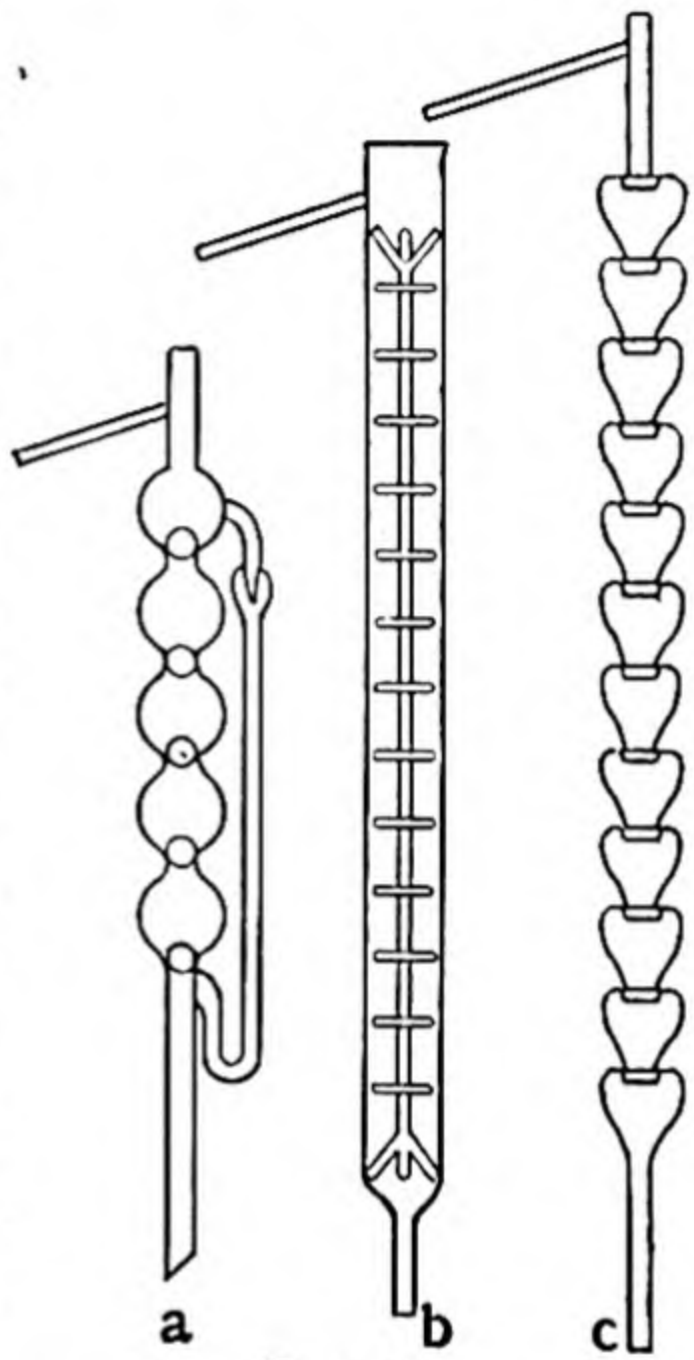


FIG. 43.

49. Ternary azeotropic mixtures. The separation of constant boiling mixtures of two liquids, such as that obtained with alcohol and water, is rendered possible by the addition of a suitable third liquid. Benzene and water, for example, are practically immiscible. Each is miscible with alcohol, and each with alcohol gives a mixture of minimum boiling point. Sidney Young* found that when any mixture of the three liquids is distilled, a ternary azeotropic mixture comes over at a temperature lower than the boiling point of either of the binary mixtures or of any of the pure substances. This ternary mixture boils at 64·85° and contains benzene 74·1, alcohol 18·5, and water 7·4 per cent. Young's original method was patented in 1903, and was discon-

* *J.C.S.* 1902, 707. *Distillation* (Macmillan and Co. Ltd.), 1922.

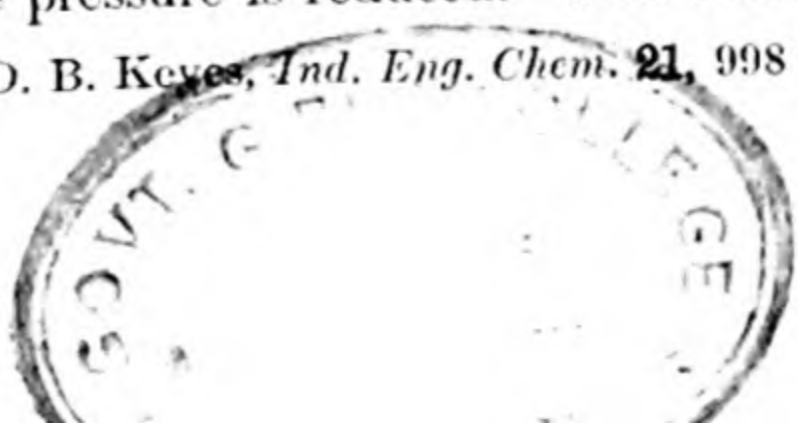
tinuous, the process being carried out in batches with addition of the required amount of benzene to give the azeotropic ratio. The continuous process for the production of anhydrous alcohol was developed on a commercial scale first in the United States.* The vapour of the ternary azeotrope, having the lowest boiling point, passes to the top of the column, from which it is led to a condenser. The liquid separates into two layers ; the lower layer contains the water and is removed, while the upper layer, consisting of benzene and some alcohol, is returned to the top of the column. Pure alcohol is drawn from the bottom of the column.

Since the beginning of the century continuous methods of distillation have become almost universal, and are applied on the industrial scale in the separation of oxygen and nitrogen from liquid air, in the distillation of petroleum, coal tar and pyroligneous acid, and in the manufacture of alcohol, ether and ethereal salts.

50. Distillation under reduced pressure. Since the boiling point of a substance is the temperature at which its vapour pressure is equal to the atmospheric pressure, a lowering of the atmospheric pressure will also lower the boiling point. This explains the advantage of distillation under diminished pressure, sometimes called vacuum distillation. When a liquid boils at an inconveniently high temperature, or decomposes when distilled at atmospheric pressure, the method of reduced pressure must be applied.

The accompanying diagram (Fig. 44) illustrates the laboratory apparatus employed for the purpose. The flask *a*, containing the liquid to be distilled, is of the double-necked type known as a Claisen flask. It has the advantage that there is less risk of the liquid splashing on to the bulb of the thermometer, which is placed in the curved neck from which the exit tube passes. The second neck carries a piece of glass tube drawn to a fine capillary which reaches as near to the bottom of the liquid as possible. Its object is to admit to the liquid a stream of minute bubbles of air as soon as the pressure is reduced. This secures regular boiling

* D. B. Keyes, *Ind. Eng. Chem.* **21**, 998 (1929).



and prevents the bumping which is especially liable to occur under diminished pressure. Instead of the Claisen flask an ordinary distilling flask may be used, provided with a two-holed stopper. Sometimes, to reduce the number of possible openings, a one-holed stopper is used and the thermometer placed within the glass tube. This arrangement is not good, because the thermometer is heated through the glass tube, and is also exposed to the current, however minute, of cool air.

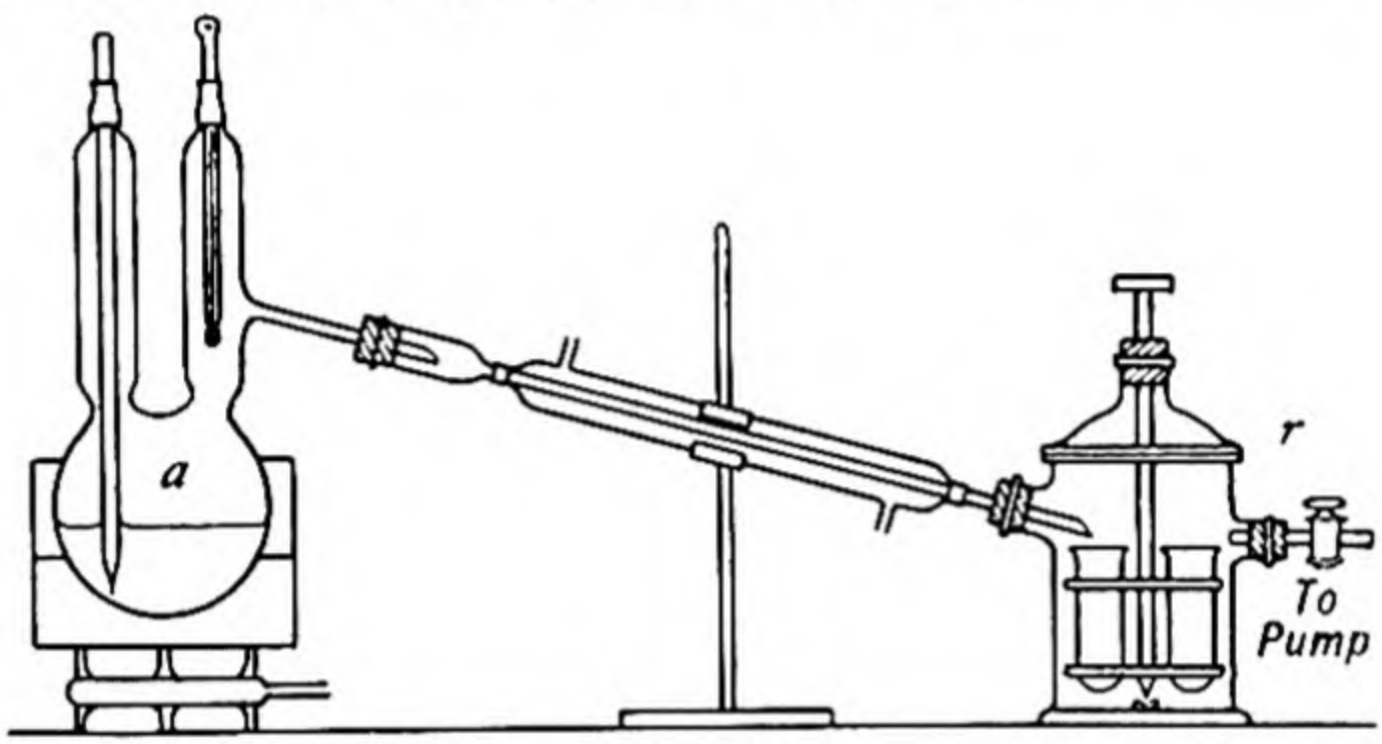


FIG. 44.

The receiver *r* contains from three to six short test-tubes in a turn-table which can be operated without opening the receiver. This provides for the collection of the distillate in fractions.

The pressure is indicated by a manometer (not shown in the diagram), and should be recorded for each reading of the temperature.

51. Extraction from aqueous solution. When a substance which has been distilled with steam, or for any other reason has been long in contact with water, is appreciably soluble in water, the portion which remains in the water is usually recovered by extraction with an immiscible solvent. This is best done in the separating funnel (Fig. 29). The solvent selected should be, if possible, quite insoluble in water, and should not dissolve water, so that it may be easily and quickly dried after the extraction. It should also be volatile, so that it may be readily distilled and recovered. Ether has the disadvantage of taking up too much

water. Hydrocarbons and their chlorinated derivatives are much used. A suitable quantity of the solvent is added to the water in the funnel, and the latter vigorously shaken. On settling, the lower liquid is run off. The extraction may be repeated as often as is deemed necessary, and the collected portions of solvent then dried and distilled to recover the substance.

52. Partition law. The principle underlying the above process is known as the partition law, or the distribution law, discovered by Berthelot and Jungfleisch in 1872. When a substance is soluble in each of two solvents which are themselves immiscible or nearly so, and has the same molecular weight in both solvents, the ratio of its concentrations in the two solvents at a given temperature is constant, and is equal to the ratio of its maximum solubilities in the two solvents respectively at that temperature. This ratio is called the distribution ratio (k). The law is analogous to Henry's law for gases. It is independent of the quantity of substance dissolved, so long as the solutions are dilute. It does not hold if the two solvents are appreciably soluble in each other, or if their mutual solubility is affected by the solute.

If the molecular weight is not the same in both solvents, the ratio of the concentrations is modified, as was shown by Nernst (1891), just as in Henry's law (42). Thus if the solute exists as simple molecules in solvent A, and as complex (n) molecules in solvent B, the partition coefficient is

$$K_1 = \frac{C_A}{\sqrt[n]{C_B}}, \quad \text{or} \quad K_1 = \frac{C_A^n}{C_B}.$$

As an example of the application of the process, suppose that we have a substance twice as soluble in benzene as in water, and that we shake equal volumes of the two solvents with a quantity of the substance insufficient to saturate them. Let s_1 and s_2 be the solubilities of the substance in water and benzene respectively, and let x be the fraction of the substance left in the water, $1-x$ that in the benzene. Then

$$\frac{x}{1-x} = \frac{s_1}{s_2} = k;$$

k is called the partition coefficient. In the case supposed this is $\frac{1}{2}$, so that

$$\frac{x}{1-x} = \frac{1}{2}, \quad \text{or} \quad x = \frac{1}{3}.$$

Thus a single extraction with an equal volume of benzene removes two-thirds of the substance from the water.

53. Number of extractions. The quantity of solvent available for extraction is usually limited, and it becomes important therefore to consider the most effective way to use a given volume, whether in one quantity or in several smaller portions. In the above example, suppose the benzene to be used in two equal portions, each, that is, half the volume of the water. The distribution ratio is now

$$k = \frac{x}{2} : \frac{1-x}{1}, \quad \text{or} \quad \frac{x}{2(1-x)} = \frac{1}{2};$$

$$\therefore \; x = \tfrac{1}{2};$$

and on repeating the extraction from the water with the second half of the benzene, the fraction then remaining in the water will be $x_2 = \frac{1}{4}$. It is therefore more efficient to use the solvent in several small portions than in one large one. This may be expressed in general terms as follows :

Let x_1 represent the fraction of the substance remaining in a volume of water v_1, and $1 - x_1$ the fraction extracted by the volume v_2 of the solvent. Then

$$\frac{x_1}{v_1} = k\frac{1-x_1}{v_2};$$

$$\therefore \; x_1 = \frac{kv_1}{v_2 + kv_1}.$$

Let a second extraction with an equal volume v_2 of the solvent leave the fraction x_2 in the water. The portion removed is therefore $x_1 - x_2$, so that

$$\frac{x_2}{v_1} = k\frac{(x_1 - x_2)}{v_2}, \quad \text{and} \quad x_2 = x_1 \cdot \frac{kv_1}{v_2 + kv_1}.$$

Substituting the above value of x_1, we have

$$x_2 = \left(\frac{kv_1}{v_2 + kv_1}\right)^2,$$

and the fraction x_n of the original substance, left in the water after n extractions with equal portions v_2 of the solvent, will be

$$x_n = \left(\frac{kv_1}{v_2 + kv_1}\right)^n.$$

On the other hand the fraction of the substance which would remain in the water if the total volume of solvent, nv_2, were used in one operation, would be

$$x = \frac{kv_1}{nv_2 + kv_1}.$$

This is clearly greater than x_n. The value of x_n will be smaller, and the difference $(x - x_n)$ will be greater, that is, the advantage of using the solvent in n portions will be greater, the smaller is the value of the coefficient k, the larger the volume v_2 of the solvent used in each extraction, and the greater the number of extractions n.

54. Solutions of solids in liquids form the great majority of those met with in practice. Here again the kinetic theory affords an explanation of the fundamental phenomena. Particles of the solid, called the *solute*, leave it and penetrate the liquid, called the *solvent*. In this they move about as do the molecules of gases in the process of diffusion, but much more slowly, colliding with the liquid molecules, with the sides of the vessel, and with the solid itself, with which they may again become incorporated. As increasing numbers of molecules leave the solid for the solution, there comes a time when the number of molecules passing from the solid to the liquid and *vice versa* in a given time is the same. There is then equilibrium between the two phases, the solid and the liquid or solution, and the concentration of solute molecules in the liquid has reached a maximum. The solution is then said to be saturated. This maximum concentration represents the *solubility*, and is constant at a given temperature, increasing usually with rise of temperature (7). These considerations are

independent of possible union between the solute molecules and those of the solvent, which in some cases does occur to a limited extent. They are also independent of, and are accompanied by, the *ionisation* of the solute molecules (75) in the case of all substances which exhibit polar properties.

55. The process of diffusion in liquids can be demonstrated by carefully placing a saturated solution of copper sulphate at the bottom of a tall jar of water. The blue colour gradually rises in the jar. If also some saturated ammonia solution is placed on the top of the water, the effects of its reaction with the copper will appear about midway in the jar. Potassium permanganate also may be used. Two beakers may be connected bridge-wise by a ∩-tube, all containing water. In one beaker some solid ferric chloride is placed, in the other thiocyanate. After a time the red colour of ferric thiocyanate appears in the bridge-tube.

56. **Osmotic pressure.** In this process of diffusion in liquids the heavier molecules move more slowly than the lighter ones. The difference was first observed, in the case of alcohol and water, by the Abbé Nollet in Paris in 1748. He filled a vessel with alcohol, closed it with a piece of bladder, and immersed the whole in water. The water entered so rapidly that the bladder was distended outwards almost to bursting. When the positions of the liquids were reversed, the opposite effect took place.

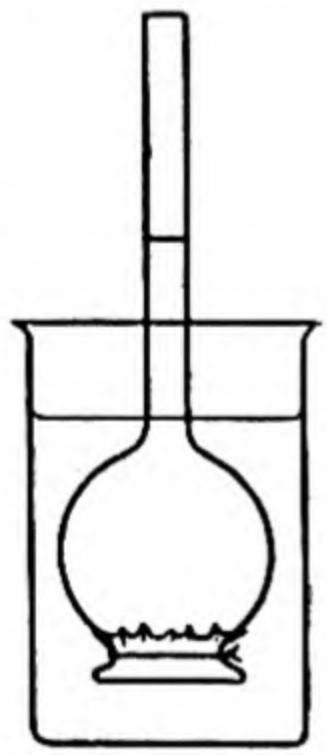


FIG. 45.

Nollet's experiment may be modified by using a thistle funnel (Fig. 45), closed with a piece of pig's bladder, and filled with alcohol to a point marked on the stem. When the funnel-head is immersed in water, the liquid rises rapidly in the tube. The effect may be rendered more easily visible by dissolving a little eosin or other coloured substance in the alcohol. A solution of cane sugar in water may be placed in the funnel, and water in the beaker. The result is similar in kind, though not so rapidly attained. Since the membrane is permeable to

alcohol and sugar molecules as well as to water, the upward movement of the liquid in the tube is not permanent, but as diffusion proceeds the composition of the liquid ultimately becomes the same on both sides of the membrane, and the level of liquid is then also the same inside and outside of the tube.

The term *osmosis* was applied by the French physiologist Dutrochet to the process of diffusion in liquids, and the resulting hydrostatic pressure came to be known as *osmotic pressure.* He also introduced the terms *endosmose* and *exosmose* for the opposite movements of liquid through cell walls. The process of *dialysis* introduced by Graham in 1861 is an application of osmosis.

A simple apparatus like the above, which may be called an *osmoscope*, merely indicates the existence of osmotic pressure. It cannot give even an approximate measure of this pressure. But we can imagine a membrane which would completely prevent the passage of solute molecules while offering no obstruction to those of the solvent. Such a membrane, which van't Hoff called a *semi-permeable* membrane, would thus induce an increase of the hydrostatic pressure in the solution until this became equal to the force causing osmosis. When this equilibrium of forces is reached, the hydrostatic pressure has attained a maximum value which is called the *osmotic pressure of the solution.* The concentration of the solution has of course been diminished by the inflow of water through the membrane. The final concentration must be considered in all discussions of osmotic pressure.

57. Measurement of osmotic pressure. Such membranes may be obtained with copper ferrocyanide, and were first successfully used by the German botanist Pfeffer in 1877 in his experimental study of osmotic pressure. Pfeffer caused the substance to be precipitated in the walls of a porous battery cell by filling the pot with copper sulphate solution and placing it in a solution of potassium ferrocyanide. He found that the gelatinous film so produced was strong enough to withstand a pressure of several atmospheres.

Pfeffer, working chiefly with sugar solutions, showed that at a fixed temperature the osmotic pressure of a solution is propor-

tional to the concentration, that is, inversely proportional to the volume occupied by a given quantity. This is exactly analogous to Boyle's law for gases. He showed further that the osmotic pressure of a solution increases in proportion to the absolute temperature, in agreement with the gas expansion law of Charles.

58. van't Hoff's theory of dilute solutions. The important results obtained by Pfeffer attracted the attention of van't Hoff, who pointed out the analogy between the behaviour of gases and that of solutions, taking the osmotic pressure of the solution in place of the gaseous pressure. On the assumption that the solutions are very dilute, or *ideal* solutions, he showed from thermodynamic considerations that the osmotic pressure of a solution is equal to the gas or vapour pressure which the dissolved substance would exert if it could exist as vapour at the same temperature and in the volume occupied by the solution. The combined gas equation

$$PV = RT$$

is therefore applicable to dilute solutions, and the value of the constant is the same for both gas and solution. The osmotic pressure is thus independent of the nature of the solute, and depends only on the molecular concentration. Solutions therefore of the same molecular concentration have also the same osmotic pressure, that is, they are *isotonic*. This is confirmed by the results obtained by Pfeffer and others.

59. Molecular weights in solution. It follows that the molecular weight of a dissolved substance can be calculated by determining the osmotic pressure of a solution of known concentration, and making use of the relationship $P = \frac{nRT}{V}$, where n is the number of gram-molecules of dissolved substance in V litres of the solution.

The osmotic pressure, however, is difficult to measure accurately, and other properties of the solution are therefore used instead.

It has long been known that the vapour pressure of a liquid is lowered by dissolving another substance in it. Wüllner's law

(1856) states that this lowering of the vapour pressure of a solvent is proportional to the molecular concentration of the solute. Solutions therefore, in the same solvent, having the same osmotic pressure, should also have the same vapour pressure. This is confirmed by experiment, and can be deduced from the van't Hoff law for dilute solutions.

The earlier work on vapour pressure of solutions made use of inorganic salts, the ionisation (75) of which complicated the results. In 1886, however, Raoult, by using solutions of organic non-electrolytes in organic solvents, established the relationship :

$$\frac{p-p'}{pg}M' = \frac{M}{100},$$

p and p' being the vapour pressures of the solvent and solution respectively, M and M' the molecular weights of solvent and solute, and g the number of grams of solute in 100 grams of the solvent. But $\frac{g}{M'}$ is the number of gram-molecules of solute (n), $\frac{100}{M}$ the same value for the solvent (N), so that

$$\frac{p-p'}{p} = \frac{n}{N}.$$

For more concentrated solutions n becomes appreciable in comparison with N, and the ratio is more correctly expressed as $\frac{n}{N+n}$. As Raoult expressed it, the relative lowering of the vapour pressure is equal to the ratio of the number of gram-molecules of solute to the total number of gram-molecules in the solution.

Vapour pressure can be used in this way for the determination of molecular weights, but it is more usual, and simpler, to find either the lowering of the freezing point of the solution or the elevation of the boiling point, which results from the lowering of the vapour pressure. In the accompanying diagram (Fig. 46) *ab* is the vapour pressure curve of the solvent, *cd* that of a solution, and *ca* the curve for ice. At the point *a* where the curves for liquid and solid solvent meet, the solid and liquid

forms have the same vapour pressure and are in equilibrium. This is the freezing point of the pure solvent. Similarly c is the freezing point of the solution, which is clearly below that of the solvent, and must be the same for all solutions in that solvent having the same vapour pressure, that is, the same molecular concentration.

For dilute solutions, the small parts of the curves involved may be taken as straight lines, and the depression of the freezing

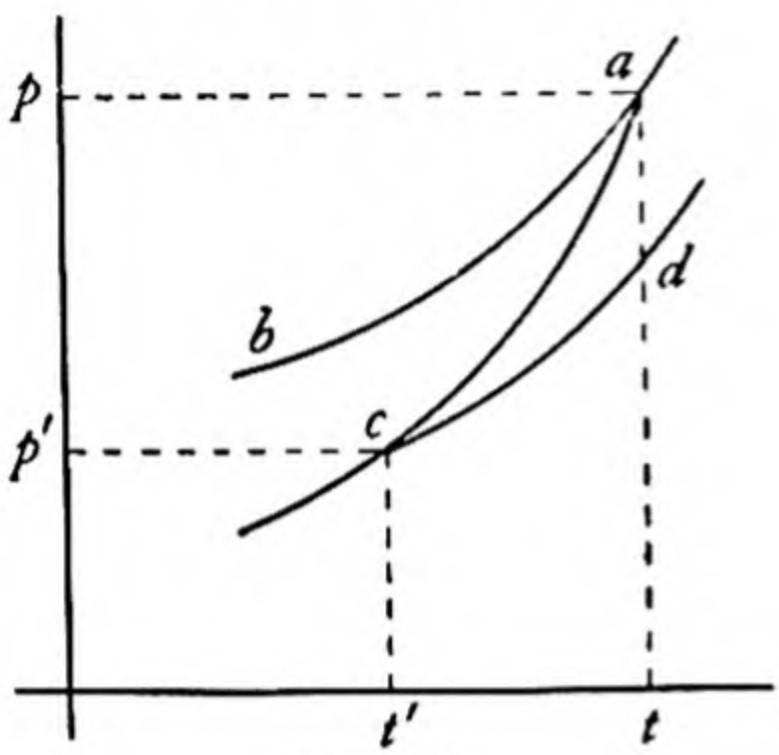


FIG. 46.

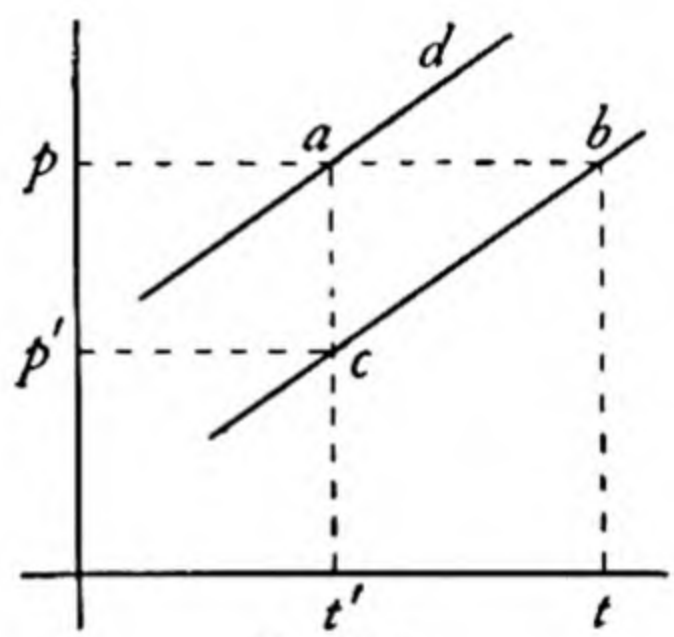


FIG. 47.

point is thus proportional to the fall in vapour pressure, or dt/dp is constant.

Dilute solutions, therefore, in a given solvent, having the same molecular concentration, have not only the same osmotic pressure, and the same vapour pressure, but the same freezing point.

This is true also of the boiling point, which is raised as a result of the lowering of the vapour pressure. Let ad and bc (Fig. 47) represent small portions of the vapour pressure curves of a solvent and a solution, which may be taken as parallel straight lines. The lowering of vapour pressure at temperature t' is ac, while ab is the increase of boiling point at the pressure p. But

$$\frac{ab}{ac} = \frac{dt}{dp} = \tan \angle acb,$$

which is constant. The increment in the boiling point of a solution is therefore also proportional to the lowering of vapour

pressure, to the molecular concentration, and to the osmotic pressure.

60. Freezing point of solutions. In 1788 Blagden showed that the lowering of the freezing point of aqueous solutions of inorganic salts is proportional to the concentration of the solution. About one hundred years later, Raoult examined solutions of sugar and other organic substances, non-electrolytes, in water and in organic solvents, and established a general law of a similar form. He found that for any given solvent, the depression of the freezing point produced by dissolving one gram-molecule of a substance in 100 g. of the solvent is constant. This constant is called the *molecular lowering* of the freezing point :

$$k = \frac{M \,.\, dt}{g},$$

where M is the molecular weight of the solute, dt the actual depression of the freezing point, and g the number of grams of solute in 100 g. of the solvent. Van't Hoff showed from thermodynamic laws that this constant is related to the latent heat of fusion (L) of the solvent, and the absolute temperature of freezing of the pure solvent (T) thus :

$$k = 0{\cdot}02\,\frac{T^2}{L}\,.$$

We therefore have

$$M\,\frac{dt}{g} = \frac{0{\cdot}02\,T^2}{L}\,.$$

This assumes that *pure solvent* separates as ice when the solution freezes. If the latent heat of the solvent is known, van't Hoff's constant can be calculated, and molecular weights found from the relation :

$$M = \frac{g}{dt}\cdot\frac{0{\cdot}02\,T^2}{L};$$

if unknown, an experimental value for the molecular depression may be found by using a substance of known molecular weight.

The values for the experimental and theoretical depressions for some common solvents are as follow :

Solvent	F.P.	k (exper.) from $M\frac{dt}{g}$	k (calc.) from $\frac{\cdot 02T^2}{L}$
Water - -	0°	18·5	18·6
Acetic acid -	17°	39·0	38·2
Benzene -	5·5°	51·2	50·7
Nitrobenzene	6°	70·7	69·5
Naphthalene	80°	71·0	69·4

Raoult referred the molecular depression to 100 g. of solvent, but many later writers have used 1000 g. On this basis the values for k in both columns would be one-tenth of those given above.

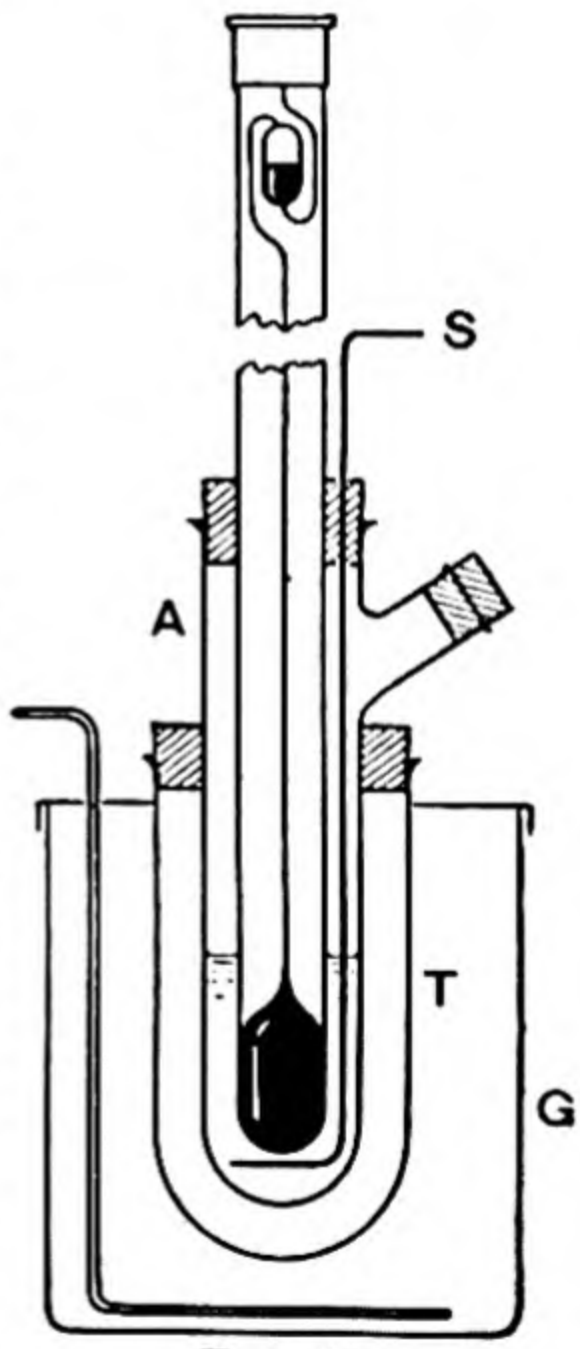


FIG. 48.

61. Beckmann's apparatus, shown in Fig. 48, is the one generally used for freezing point determinations. The tube A contains the solvent, of which 23–30 g. are accurately weighed. This tube is supported in a wider tube T, so that it is not in direct contact with the cooling medium in the outer glass jar G. A delicate thermometer, usually of the special Beckmann type (63), and the stirrer S, are supported in A. The outer jar is filled with a freezing mixture of crushed ice and salt water, and the solvent in A is gently stirred from time to time until ice begins to separate. The liquid is then stirred briskly to ensure thorough mixing of the ice and solvent, and the temperature is carefully noted. The tube is then withdrawn and the ice melted. A weighed crystal or pellet of the substance to be examined is now introduced by the side tube, and is dissolved by

stirring. Again the freezing point is determined. The liquid usually becomes supercooled in this process, and rapid stirring is resorted to in order to promote the separation of ice. When this begins, there is a rise of temperature, followed by a steady fall. The maximum temperature is taken as the freezing point. This observation may be repeated by removing A, melting the ice, and again cooling.

The following example will illustrate the method of calculating a molecular weight. 0·3183 g. of camphor dissolved in 33·99 g. of benzene caused a depression of 0·315° in the freezing point. The molecular weight is therefore

$$M = \frac{g}{dt} \times 5{\cdot}07 = \frac{0{\cdot}3183 \times 1000}{0{\cdot}315 \times 33{\cdot}99} \times 5{\cdot}07$$

$$= 150{\cdot}7.$$

Calculated for $C_{10}H_{16}O = 152{\cdot}0$.

62. The molecular elevation of the boiling point of a solvent is given by a similar expression, the van't Hoff constant in this case involving the latent heat of vaporisation (L) of the solvent. The assumption is required further that the solute is not appreciably volatile at the boiling point of the solution, and the method is therefore not applicable to the determination of the molecular weights of low boiling liquids.

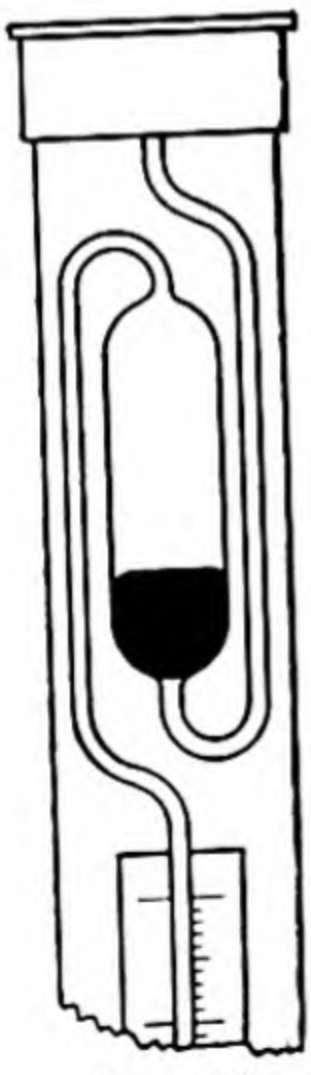


FIG. 49.

63. The Beckmann thermometers used in this and in the boiling point method described below have a reservoir of mercury (Fig. 49) at the upper end of the capillary. By bringing the thread into contact with the mercury in this reservoir, the quantity actually in use may readily be adjusted to suit liquids with different freezing or boiling points. The scale covers about six degrees. It is divided into hundredths, and may be read to thousandths of a degree, preferably by means of a telescope.

64. Beckmann's apparatus. In determining the boiling point of a liquid, the thermometer is always placed in the vapour (26), so that the temperature registered is that at which the condensed liquid on the bulb of the thermometer is in equilibrium with the saturated vapour. This is the true boiling point. But in the case of a boiling solution this method would give the boiling point of the pure solvent. The bulb of the thermometer must therefore be immersed in the liquid, and superheating must be carefully guarded against. In the Beckmann apparatus (Fig. 50) the solvent is contained in the boiling tube *A*, 2·5–3 cm. in diameter. This has a platinum stud, *S*, sealed through the bottom, to convey heat rapidly to the liquid and promote a regular formation of bubbles of vapour. Beckmann filled the lower part of the tube with garnets or glass beads, to distribute the bubbles and so better to ensure equilibrium between the boiling liquid and its vapour. The side tube serves to introduce the solute, and carries a small condenser to prevent loss of solvent.

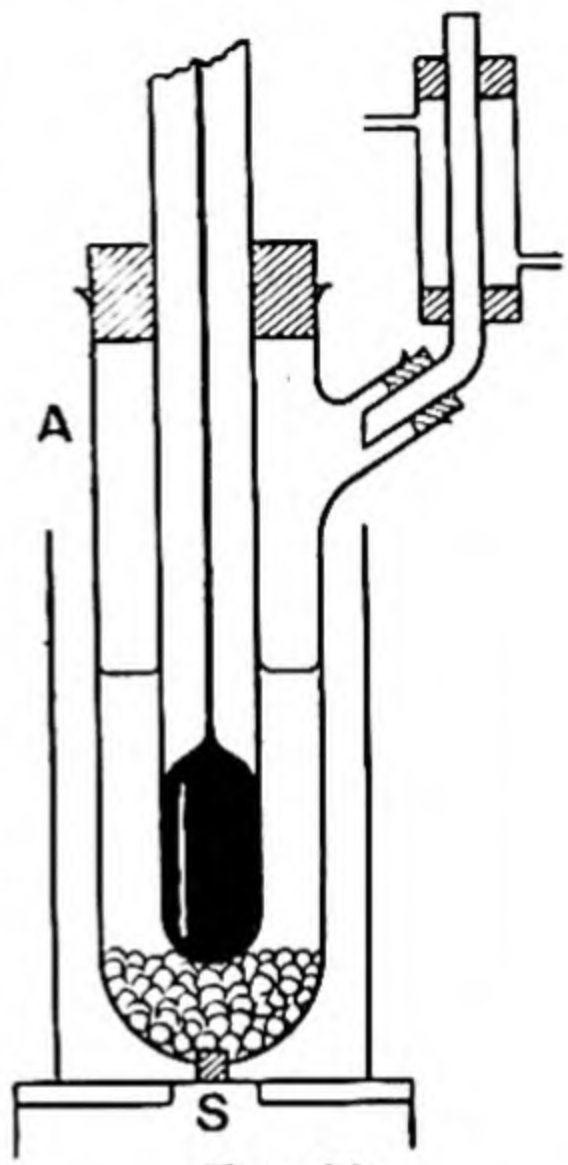


FIG. 50.

The boiling tube must also be screened from draughts, to avoid cooling, either by means of asbestos casing, or better, by a double cylindrical vessel containing the boiling solvent, as in the original Beckmann apparatus.

Electrically heated tubes have now largely replaced the older forms of gas-heated vessels. In these a small platinum coil connects the ends of two stout copper wires which pass through the cork, parallel with the thermometer, to the bottom of the liquid in *A*. This method was introduced by Bigelow in America (1899), and is more regular, rapid and accurate than the older methods. A Dewar vacuum vessel serves well in this case as a heat insulator.

Cottrell's apparatus,* modified by Spencer and others, is more

* *J. Amer. C.S.* 41, 721 (1919).

complicated. The bulb of the thermometer is held in the vapour zone in *A*, the object being to approach the conditions under which the boiling point of a pure liquid is determined. A funnel placed over the heating stud or coil is continued upwards in a tube which divides below the thermometer into two or more branches, running parallel with the thermometer to the lower part of the stem. Bubbles of vapour pass up the funnel tube and carry with them small portions of the boiling liquid, which is thus continually sprayed over the bulb. It is claimed that the method is both rapid and accurate.

65. Indirect heating, by means of a stream of vapour from the boiling solvent, was introduced by Sakurai in Japan (1892) and by Landsberger in Germany (1898). All risk of superheating is thereby avoided, and the solution is weighed *after* the boiling point has been determined. In Walker and Lumsden's modification * of the Landsberger apparatus, a graduated boiling tube is used and the *volume* of the solution is measured instead of the weight. Several determinations can thus be made with the same portion of solute, at progressively greater dilutions. Walker claimed that the method is rapid and suitable for preliminary work, with a degree of accuracy similar to that of the Victor Meyer vapour density method.

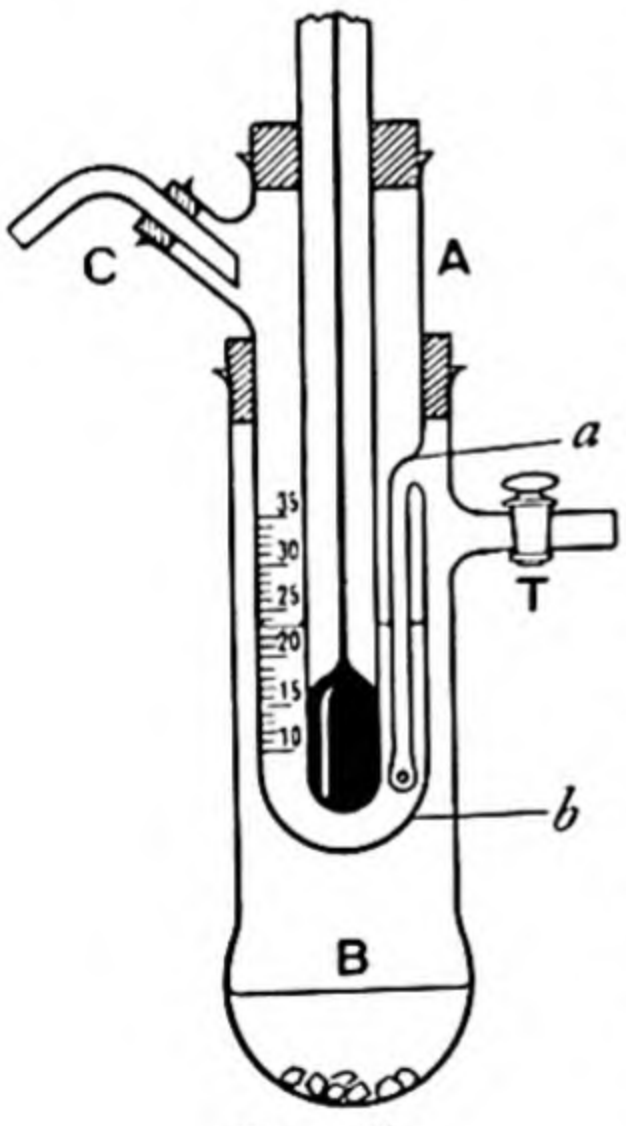


FIG. 51.

McCoy's apparatus † is one of the best of those working on this principle. The boiler *B* supplies the vapour of the boiling solvent, which first heats the solvent in the graduated boiling tube *A* (Fig. 51), provides a vapour jacket for *A*, and passes down the narrow tube *ab* into the liquid, which is thus soon caused to boil. The tube *ab* ends in a small bulb with

* *J.C.S.* 73, 502 (1898).

† *Amer. Chem. J.* 23, 353 (1900).

several holes by means of which the vapour is distributed. Excess of vapour is conveyed to a condenser through the side tube C, which also serves for the introduction of the solute. When the boiling point of the pure solvent has been determined, the tap T is opened and the boiling discontinued. The weighed quantity of solute is then introduced and the boiling point determined as before. The volume of the solution must then be read, after carefully removing the thermometer, and further determinations may be made either with the same quantity of solute or after adding more.

When the volume of the solvent is measured, as in the above methods, the molecular elevation of the boiling point is calculated from a concentration expressed in grams per litre, and the constant becomes $K' = K/d$, where d is the density of the solvent at its boiling point. The following table gives the values of K and K' for some common solvents, together with the value calculated by van't Hoff from the latent heat :

Solvent	B.P.	$K = M\frac{dt}{g}$	$K' = \frac{K}{d}$	$\frac{0{\cdot}02T^2}{L}$
Water - -	100°	0·52	0·54	0·515°
Alcohol - -	78·4°	1·17	1·55	1·15°
Ether - -	35°	2·10	3·02	2·11°
Acetone - -	56·3°	1·70	2·20	1·72°
Benzene - -	80·5°	2·57	3·15	2·67°
Chloroform -	61°	3·79	2·80	3·76°

CHEMICAL EQUILIBRIUM

66. In analytical chemistry great use is made of reactions in which a substance is precipitated on mixing two solutions. Its colour, density, texture and other properties serve for the identification or for the estimation of an element or radical. For example, if equivalent solutions of barium hydroxide and sulphuric acid are mixed together, an immediate and complete precipitation of barium sulphate occurs :

$$Ba^{\cdot\cdot} + 2OH' + 2H^{\cdot} + SO_4'' \rightarrow BaSO_4 + 2H_2O.$$

Such reactions appear to take place instantaneously, and support the early conception of Bergman (1775) in regard to chemical affinity, that a reaction proceeds in one direction only. But in such cases the substance precipitated is removed from the system in which the reaction occurs, by reason of its insolubility, and the reaction is therefore not of the simplest type.

If we consider a homogeneous system, one, that is, which has the same chemical and physical nature at all points, such as a mixture of gases or a solution, we find that the equilibrium, or balance of opposing tendencies, referred to previously in the case of a liquid and its vapour, or a solute and its solution, is also characteristic of most chemical reactions. The simplest of these occur among gases. When hydrogen and iodine (vapour) are heated together, hydrogen iodide is formed, and the reaction, which is very slow at moderate temperatures, reaches an equilibrium or balanced state in a few hours at the temperature of boiling sulphur (445°) :

$$H_2 + I_2 \rightleftharpoons 2HI.$$

The reaction is incomplete, some of the elements remaining free ; and when hydrogen iodide itself is heated under similar conditions, it is to some extent decomposed into the elements. The reaction is therefore a reversible one. In all such reactions, if equivalent quantities of the reactants be used, the equilibrium reached under constant conditions is the same from either side.

The first suggestion of the influence of mass or concentration on a reaction was made by Berthollet in 1803, who said that " every substance . . . acts by its affinity *and its mass* ". Bunsen (1853) exploded mixtures of carbon monoxide and hydrogen with oxygen insufficient to unite with all the combustible gas. He found that the amount of oxygen taken by each gas depended on the relative proportion of that gas in the mixture. J. H. Gladstone (1855) studied the reaction between potassium thiocyanate and ferric chloride, using colour intensity of the ferric thiocyanate as indication of the extent of the reaction :

$$FeCl_3 + 3KSCN \rightleftharpoons Fe(SCN)_3 + 3KCl.$$

He found that the maximum colour in dilute solutions was not produced with equivalent quantities, but only when an excess of one or other of the reactants was used, the volume of course being kept constant.

THE LAW OF MASS ACTION

67. The first definite statement of the part played by concentration in chemical reactions was made by the Norwegian chemists, Guldberg and Waage, in 1867. It may be expressed in the following way :

The law of mass action. The velocity of a chemical reaction is proportional at any moment to the active mass of each of the substances taking part in the reaction.

The " active mass " is the molecular concentration of the substance in unit volume of the chemical system. It is given by the number of grams of substance in unit volume divided by the molecular weight.

The law was developed by Guldberg and Waage from the kinetic view of chemical reactions. If two substances, A and B, can react with each other to produce two others, C and D, which again are capable of interaction under similar conditions to reproduce the original bodies :

$$A + B \rightleftharpoons C + D,$$

it is clear that the reaction of A with B can take place only during contacts of their separate molecules, and although each contact does not necessarily result in a reaction, it is assumed that the velocity of the reaction is proportional to the frequency of collisions between A and B. But the frequency of collisions is, on the kinetic theory, proportional to the product of the concentrations of the molecules, and thus the velocity of the reaction, or the amount of material changed in unit time, is proportional to the product of the molecular concentrations or active masses of the substances taking part in the change. The temperature must remain constant, for a change in temperature will affect the speeds of the molecules and therefore also the frequency of the collisions.

If we represent the concentrations of the molecular species A, B, C and D by $[A]$, $[B]$, $[C]$ and $[D]$, and the velocities of the direct and the reverse reactions by v_1 and v_2, then we have

$$v_1 = k_1[A] \times [B] \quad \text{and} \quad v_2 = k_2[C] \times [D],$$

where k_1 and k_2 are constants depending on the temperature and on the nature of the reactants, which includes the probability of their reaction on contact of the molecules.

The total velocity of reaction in this mobile equilibrium will be $V = v_1 - v_2$, and when the equilibrium condition is reached, $v_1 = v_2$ and $V = 0$. Hence

$$k_1[A] \times [B] = k_2[C] \times [D]$$

and

$$\frac{k_1}{k_2} = \frac{[C] \times [D]}{[A] \times [B]} = K.$$

K is called the equilibrium constant of the reaction. It is independent of the concentrations, and dependent only on the nature of the reaction, and on the temperature. The law has been verified experimentally, and the value of the equilibrium constant found, in a great many cases.

68. Homogeneous equilibrium. A classic example is found in the interaction of alcohol and acetic acid. When these are mixed together, ethyl acetate and water are slowly formed, the first being evident by its fruity odour. If, on the other hand, ethyl acetate and water are mixed under the same conditions, the liquid, which is at first neutral, begins to develop acidity, free acetic acid and alcohol being formed. The reaction is, in fact, reversible, and may be followed experimentally from either side by estimating, at intervals of time, the amount of free acid in small test portions. This diminishes in the direct reaction (v_1), increases in the reverse (v_2), while the concentrations of the other reactants change accordingly; but it becomes constant at the equilibrium point, which is thus recognised:

$$CH_3COOH + C_2H_5OH \underset{v_2}{\overset{v_1}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O.$$

The reaction was carefully studied by Berthelot and L. Péan de St. Gilles (1862–63), who showed that in order to convert the whole of a given quantity of acid into the ester, as the compound is called, a large excess of alcohol is required, and *vice versa*, and the quantity of ester produced increases with the excess of the acid or the alcohol. This effect of mass action may be stated generally in the following way. Suppose that one gram-molecule of acetic acid is mixed with m gram-molecules of alcohol, and that x is the fraction of a gram-molecule of ester in the resulting equilibrium mixture. The quantities of acid, alcohol and water at equilibrium will therefore be $(1-x)$, $(m-x)$ and x. If v be the volume of the mixture in litres, the molecular concentrations will be

$$\underset{\frac{1-x}{v}}{CH_3COOH} + \underset{\frac{m-x}{v}}{C_2H_5OH} \rightleftharpoons \underset{\frac{x}{v}}{CH_3COOC_2H_5} + \underset{\frac{x}{v}}{H_2O}$$

and the equilibrium coefficient, as in the example above, will be :

$$K = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{1-x}{v} \times \frac{m-x}{v}} = \frac{x^2}{(1-x)(m-x)}.$$

For equivalent quantities of acid and alcohol, at 100°, they found that equilibrium is reached when two-thirds of the material is transformed ; the equilibrium coefficient is therefore

$$K = \frac{(\frac{2}{3})^2}{(\frac{1}{3})^2} = 4.$$

The validity of the law of mass action in this reversible process is indicated by the constancy of this coefficient for all values of m. It is only slightly influenced by temperature, although the actual velocity of the reaction is greatly increased by increase of temperature. At 10° the limit of esterification is 65·2 per cent. ; at 100° it is 66·6, and at 220°, 66·5.

Another test of the validity of the law is to employ the experimental value of K in the above case to calculate the value of x for different values of m. Some results obtained by Berthelot

and St. Gilles are given in the adjoined table; the agreement between the theoretical and the experimental results is very close.

m	x observed	x calculated
0·05	0·05	0·049
0·18	0·171	0·171
0·33	0·293	0·311
0·50	0·414	0·423
1·00	0·667	0·667
2·00	0·858	0·845
8·00	0·996	0·945

Similar considerations apply to all reactions of this type, each having its own characteristic constant.

It is evident from the above considerations that the removal of one of the products will extend the course of the direct reaction. This is done in practice by the removal of water by means of a dehydrating agent, to increase the yield of ester (206). On the large scale volatile esters are removed by continuous distillation, with the aid of a column (49).

In the above reaction K is independent of the volume, and therefore the equilibrium is not influenced by dilution with an indifferent solvent. This is no longer true, however, if the number of molecules is changed by the reaction.

69. Hydrogen iodide. When two or more molecules of one substance take part in a reaction, they are equally involved in the formation of the product. The velocity of the reaction is therefore proportional to the total concentration of that substance raised to the power indicated by the number of molecules engaged. In the case of hydrogen iodide, for example:

$$2HI \quad \text{or} \quad HI + HI \rightleftharpoons H_2 + I_2$$

and the velocities

$$k_1[HI] \times [HI] \quad \text{or} \quad k_1[HI]^2 = k_2[H_2] \times [I_2],$$

therefore

$$K = \frac{k_1}{k_2} = \frac{[H_2] \times [I_2]}{[HI]^2}.$$

In Bodenstein's experiments (1897) on this reaction the coefficient K was found to vary only within the limits of experimental error. Concentrations are expressed in gram-molecules per litre.

Lemoine showed (1877) that the equilibrium in this reaction is independent of the external pressure. This would be expected; for, let the pressure be increased n times; then, according to Dalton's law of partial pressures, the partial pressure, or concentration, of each constituent is increased n times, so that

$$K = \frac{n\,[H_2] \times n\,[I_2]}{n^2[HI]^2} = \frac{[H_2] \times [I_2]}{[HI]^2}.$$

This is true also of the introduction of an indifferent gas, either at constant volume or at constant pressure, and applies to all reactions among gases in which the total number of molecules is not altered. Such cases are comparable with that of ethyl acetate, and are not influenced by dilution.

70. Le Chatelier's theorem. When the number of molecules does change in the course of a reaction, the equilibrium constant is affected by a change of volume, that is, of pressure in the case of gases, or by dilution in the case of gases, liquids or solutions. Such effects, and those also of changes of temperature, can be predicted qualitatively by Le Chatelier's theorem (1884): when a change occurs in one of the factors controlling a state of equilibrium, the equilibrium moves in the direction which tends to counteract the change. Thus an increase of pressure will cause the reaction to proceed in the direction consistent with a smaller volume, and *vice versa*. If no change of volume results from the reaction, as in the case of hydrogen iodide, the equilibrium constant is not affected by a change of pressure. An increase of temperature will shift the equilibrium so that an absorption of heat takes place. High temperatures therefore favour endothermic reactions; low temperatures favour exothermic reactions. The change in the equilibrium constant can be calculated from the equation:

$$\frac{d \log K}{dT} = -\frac{Q}{RT^2},$$

Q being the heat evolved in the reaction.

Henry's law (42) affords a simple example of the kind of change predicted by the Le Chatelier theorem. An increase of pressure in the system—gas + solvent—causes the equilibrium to change in accordance with a smaller volume ; that is, more gas dissolves.

The synthesis of ammonia illustrates the effects of changes in both pressure and temperature :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

In this reaction the number of molecules, and hence the volume, is halved ; the production of ammonia will therefore be increased by an increase of pressure. The equilibrium constant is :

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}.$$

Since the reaction also is exothermic, the formation of ammonia will be greater at relatively low temperatures. These predictions are borne out by the manufacturing conditions in the Haber process. At higher temperatures, or at lower pressures, than the working optima, the yield of ammonia diminishes. See also the synthesis of methanol (190).

71. Thermal dissociation. The decomposition of hydrogen iodide into its elements on heating is an example of a common phenomenon known as thermal dissociation. An example of another type is found in ammonium chloride, which is formed by the union of the gases ammonia and hydrogen chloride, unless these are perfectly dry (Baker), and is decomposed again, or dissociated, into the component gases on heating :

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

Here we may assume the dissociating ammonium chloride to exist as vapour. If the partial pressures be p_1, p_2 and p_3 respectively, the coefficient of equilibrium is

$$K = \frac{p_2 p_3}{p_1}.$$

In presence of solid ammonium chloride, the partial pressure p_1 is constant, in which case the constant $K' = p_2 p_3$.

If such a partially dissociated substance be compressed without change of temperature, each partial pressure is increased in the same proportion, and the coefficient becomes

$$K'' = \frac{np_2 \times np_3}{np_1} = nK.$$

The dissociation is therefore retarded. This is in accordance with Le Chatelier's theorem, and is found in salts like phosphonium chloride, which can be formed at ordinary temperatures only by compressing the gases :

$$PH_3 + HCl \rightleftharpoons PH_4Cl.$$

72. Abnormal vapour densities. If the mixture undergoing dissociation have some indifferent gas, that is, one which has no chemical action upon any component of the mixture, added without change of volume, then there is no change in the degree of dissociation. For, according to Dalton's law of partial pressures, the addition of another gas at constant volume does not affect the partial pressures of those already present, and the equilibrium constant is therefore unchanged. But if the indifferent gas be added at constant pressure, it then acts as a diluent, and the dissociation increases with increase of volume, in accordance with the Le Chatelier theorem. This happens, for example, in the determination of vapour densities of dissociable substances by displacement of air, in Victor Meyer's method (30). The dissociation increases with the amount of diffusion of the vapour into the air of the vessel, and very irregular values for the density are found. Ammonium chloride gives such abnormal values, and phosphorus pentachloride is another case in point. From the actual values of the vapour density, or the vapour pressure if that is being measured, the degree of dissociation, that is, the proportion of molecules split up, can be calculated.

Let each molecule dissociate into n parts, and let the fractional number of molecules dissociated be x ; then the total number of molecules in the dissociated mixture will be

$$1 - x + nx \quad \text{or} \quad 1 + (n-1)x,$$

instead of one molecule if no dissociation occurred. The vapour pressure will therefore be increased $[1+(n-1)x]$ times, and the vapour density will be $1/[1+(n-1)x]$ that of the undissociated substance. From this x may be calculated. Take the case of phosphorus pentachloride. The molecular weight is 208·4:

$$\underset{1-x}{PCl_5} \rightleftharpoons \underset{x}{PCl_3} + \underset{x}{Cl_2}.$$

Here $n=2$. The vapour density at 200° C. is 67·41, therefore

$$\frac{1}{1+x}=\frac{67\cdot41}{104\cdot2},$$

and

$$x=\frac{104\cdot2-67\cdot41}{67\cdot41}=0\cdot54,$$

that is, 54 per cent. of the molecules are dissociated.

73. Influence of one of the dissociates. If the dissociating substance is vaporised, not into an indifferent gas, but into an atmosphere of one of its own dissociates, while the volume remains constant, then the law of mass action indicates a reduction in the degree of dissociation. In the case of phosphorus pentachloride, let a quantity of chlorine be added, at constant volume,

$$\underset{p_1}{PCl_5} \rightleftharpoons \underset{p_2}{PCl_3} + \underset{p_3}{Cl_2}$$

whose partial pressure alone would be α. The total pressure of chlorine is thus increased, and if the value of K is to remain constant, the partial pressure of the pentachloride must increase. Let this increase be β. The partial pressures of the dissociates are each reduced by the same amount, so that we have

$$K=\frac{(p_3+\alpha-\beta)(p_2-\beta)}{p_1+\beta}.$$

The values of p_1, p_2, p_3, α and K are positive, and if the equation be solved for β in terms of these, β also is found to be positive. Thus the addition of one of the dissociates, at constant volume, retards the dissociation.

In the simpler case where solid pentachloride is present, p_1 is constant, and therefore $p_2\,p_3$ also is constant. If p_3 be increased,

p_2 must diminish ; more solid pentachloride therefore is formed—that is, the dissociation is retarded.

If the dissociate be added at constant pressure, however, it has the effect also of a diluent, which increases dissociation. There may thus be either an increase or a decrease of dissociation, according to conditions. If the pressure of the added chlorine is just equal to its partial pressure in the mixture, there will be no change in the degree of dissociation. But in applying this modified procedure to Victor Meyer's vapour density method, the pressure of chlorine in the tube (*A*, Fig. 37) is much greater than this partial pressure, and the effect should be to diminish or prevent the dissociation. This is borne out by experiment.

74. Heterogeneous equilibrium. The above considerations apply to all cases in which a solid substance dissociates into two gases, and therefore to all ammonium salts, substituted ammonium and phosphonium salts. A simple modification of the equation of equilibrium is required if the gases are produced in unequal volumes, as from ammonium carbamate :

$$NH_2 . COONH_4 \rightleftharpoons CO_2 + 2NH_3$$

and

$$Kp_1 = p_2 p_3^2.$$

All cases in which the reacting substances are present in more than one phase, gas, liquid or solid, are classed as heterogeneous equilibria.

Calcium carbonate presents an important example. Here the gas, carbon dioxide, is in equilibrium with two solids :

$$\underset{p_1}{CaCO_3} \rightleftharpoons \underset{p_2}{CaO} + \underset{p}{CO_2}$$

and

$$Kp_1 = pp_2.$$

Since the partial pressures of the solids are constant, however small, p also is constant at any given temperature. It is called the *dissociation pressure* of the carbon dioxide. It increases with increase of temperature, and reaches one atmosphere about 900°.

The law of mass applies to reactions in solutions, as well as to

those occurring among gases and liquids, and interphase reactions. But it is not valid in gas reactions at high pressures, for example, in the synthesis of ammonia, where K is far from constant, nor in solutions of high concentration. The failure is due to unknown interference with reactions owing to the close packing of molecules, but a fuller knowledge of the true nature of solutions is required before the necessary modifications in the theory can be made. There are similar failures in the application of the law to aqueous solutions of strong electrolytes (77).

IONISATION

75. It has been already pointed out (59) that solutions of inorganic salts do not behave normally in regard to the depression of the freezing point. The abnormally high osmotic pressures of such solutions were first observed by the Dutch botanist de Vries (1888) in experiments with plant cells. He introduced the term *isotonic coefficient* (i) to express the relation between the actual values and those of a normal substance at equivalent concentration. The abnormality is found in all cases to increase with the degree of dilution. Soluble substances may be divided into two classes, which are sharply distinguished by their behaviour when dissolved :

(a) The substance dissolves without change, the molecules being unaltered and behaving in dilute solution as do the molecules of gas in a confined space. Such substances, for example cane sugar in water, obey the laws of dilute solutions, which are similar to the ideal laws of gases. Solutions of this nature do not conduct the electric current, that is, they are non-electrolytes.

(b) The substance in solution gives abnormally high values for the osmotic pressure and other physical properties of dilute solutions ; more molecules appear to be present than are to be expected on the assumption that the substance dissolves without change.

Arrhenius * showed that such abnormal solutions conduct the electric current ; they are electrolytes. Further, if a substance which in water gives abnormal values for the osmotic pressure be

* *Z. Phys. Chem.* **1**, 621 (1887).

dissolved in another solvent in which it behaves normally, it also loses its power of conducting electricity. The parallelism between electric conductance and abnormal physical properties of solutions led Arrhenius to the theory of *electrolytic dissociation*, which assumes that when an electrolyte is dissolved, it immediately divides or dissociates partially or completely into positively and negatively charged particles or *ions*—the term first used by Faraday in 1834. This dissociation does not depend on the passage of a current, but is the cause of the conductance of the solution when a current is passed through it. The conductance of the solution, Λ, is made up of the conductances, or mobilities, of the ions :

$$\Lambda = l_a + l_c.$$

The equivalent conductance, that of a solution containing one gram-equivalent of the solute between electrodes of any size one cm. apart, increases with dilution to the degree, called *infinite dilution*, beyond which there is no further increase. This was explained by Arrhenius on the view that dilution causes an increase in the degree of dissociation, which at infinite dilution was to be presumed complete. He proposed to calculate the fraction, α, of an electrolyte which is ionised, by comparing the actual conductance with its limiting value at infinite dilution : $\alpha = \Lambda/\Lambda_0$.

Van't Hoff described the ionised and unionised molecules as *active* and *inactive* respectively. He supposed that at great dilution all the molecules of an electrolyte became active, and he used the letter i to express the ratio of the actual osmotic pressure of a solution to the value which it would have had had no dissociation occurred. This ratio, called the van't Hoff factor, may be deduced not only from osmotic pressure measurements, but also from the freezing point, vapour pressure, or equivalent conductance of the solutions. It is the same as the isotonic coefficient of de Vries, and increases with dilution.

The substances which give such electrolytic solutions are salts, acids and bases. The original theory of Arrhenius has been modified in some respects, and at the same time placed on a more satisfactory basis, by the development of the electronic theory of the constitution of matter and the results of X-ray analysis of

crystals. It is now believed that in a crystal, for example, of sodium chloride, the ions of sodium and of chlorine, formed by the transfer of one electron from the atom of sodium to that of chlorine, already exist in electrostatic equilibrium, firmly held within the crystal lattice. When the salt is dissolved, the ions move independently of one another, or dissociate. Similarly, when the salt is fused, the ions are free to move, and the liquid is a conductor. It is well established that fused electrolytes obey Ohm's and Faraday's laws, with certain reservations, just as do their aqueous solutions.

76. Ostwald's dilution law. On the assumption that ionic dissociation is reversible, the law of mass action has been extended to cover this type of reaction. In the case of uni-univalent salts, we have

$$MX \rightleftharpoons \mathrm{M}^{\cdot} + \mathrm{X}',$$

and the equilibrium constant, K, may be calculated as in other reactions (67). If C be the total concentration of the salt, and α the fractional number of molecules ionised, the concentration of each ion will be αC, and that of the unionised salt $C(1-\alpha)$. Thus

$$K = \frac{\alpha C \,.\, \alpha C}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}.$$

This is known as Ostwald's dilution law.* It is true for very dilute solutions, especially of weak electrolytes, and K is then a function of the temperature only. But at higher concentrations K is affected also by the concentration, and has no constant value. Strong electrolytes, which even in the solid form have a polar structure, do not obey the law, and many attempts have been made to explain their anomalous behaviour.

G. N. Lewis † proposed to replace the term *concentration*, in the case of electrolytic solutions, by the *activity*, a, this being the product of the concentration and the *activity coefficient*, f, the value of which varies with the concentration: $a = f \,.\, c$. The activity is proportional to the true active mass of the solute. Calculated on this basis, the value of K is fairly constant.

* *Z. Phys. Chem.* **2**, 270 (1888).

† *Ibid.*, **61**, 129 (1907).

77. Strong electrolytes. Complete dissociation of a salt in solution would appear to be a reasonable expectation from the electronic conception of the molecule, and would place the reaction beyond the range of the equilibrium law; there would then be no question of agreement, though others would arise. It was suggested by W. Sutherland * before the development of the electronic theory, for strong electrolytes at all concentrations. He pointed out that the dielectric constant must be taken into account, and that certain resistances to the free movement of the ions, mainly of an electrical character, were to be anticipated.

S. R. Milner † suggested that owing to the electrical charges on the ions each ion will be surrounded by an atmosphere of attracted particles, which will interfere with the distribution and the mobility of the ions.

Debye and Hückel ‡ based on this idea of the ionic atmosphere a theory of the complete dissociation of strong electrolytes, and proposed to explain the increase in equivalent conductance which occurs on dilution as due to increases in the mobilities of the ions, and not to any increase in the number of molecules ionised. The conductance ratio Λ/Λ_0 is thus a ratio of ionic mobilities. L. Onsager in 1926 pointed out that in calculating the retardation of an ion by its ionic atmosphere, Debye and Hückel had considered the ion as moving with constant velocity, and had ignored its Brownian movement. He added a correction for this. The conductivities of dilute solutions of uni-univalent salts in various solvents agree well with the requirements of the Debye-Hückel-Onsager equation.

The mobilities of the ions are influenced by several factors, some of which are indicated briefly in what follows.

78. Viscosity. Water is the most important and the most powerful ionising solvent. The ions of an electrolyte were at first supposed to move freely through the solution, the solvent molecules remaining unaffected by this movement or transport of the ions. But the viscosity of the liquid involves a resistance to

* *Phil. Mag.* **3**, 161 (1902); **12**, 1 (1906).
† *Ibid.* **23**, 551 (1912). ‡ *Phys. Zeits.* **24**, 185 (1923).

the passage of the ions, as was first suggested by Wiedemann in 1856. The mobility of the ions depends on the fluidity (the reciprocal of viscosity) of the medium, and in very dilute aqueous solutions the equivalent conductance of many salts is, in fact, directly proportional to the fluidity between 0° and 36°. This relationship is generalised in Walden's rule,* that the equivalent conductance of a solution at infinite dilution is inversely proportional to the coefficient of viscosity (η) of the solvents :

$$\Lambda\eta = \text{constant.}$$

The value of the constant is independent of the nature of the solvent. The rule is so closely followed, especially in the case of certain large organic ions, that ionic mobilities have been calculated from the constant and the known viscosity of a solvent.

79. **Solvation.** The effect of viscosity is increased by the association of ions with molecules of the solvent. Kohlrausch † suggested that an ion is surrounded by an atmosphere of the solvent which moves with it against a frictional resistance that increases with its size, this depending on the nature of the ion. Proof of this has since been obtained. The mobilities of the ions of the alkali metals were found to increase with increasing atomic weight, whereas the reverse would be expected. If, however, the lighter ions are combined with more water molecules, or more fully hydrated, than the heavier ones, the retardation of their movement is explained. Since similar effects occur in non-aqueous solvents, the phenomenon is indicated by the more general term *solvated*. Water possesses this solvating power to a greater degree than any other solvent. It is a general property of associated liquids.

Transference experiments have revealed changes of concentration of non-electrolytes, around the electrodes, when alkali chlorides in the same solution were electrolysed. Buchböck ‡ first obtained results by this method, using hydrochloric acid

* *Z. Phys. Chem.* **107,** 219 (1923).
† *Proc. Roy. Soc. A*, **71,** 348 (1903).
‡ *Z. Phys. Chem.* **55,** 563 (1906).

with mannitol or resorcinol as the reference substance. Washburn * used alkali chlorides with raffinose, an optically active sugar, and measured the optical rotation of the solution near the electrodes before and after the electrolysis. The changes in concentration are attributed to the transport of water molecules by the ions. Washburn calculated that if the hydrogen ion is assumed to carry one molecule of water, the relative numbers of molecules associated with other ions are, for

$$Cl' \ 4, \ Li^{\cdot} \ 14, \ Na^{\cdot} \ 8{\cdot}4, \ K^{\cdot} \ 5{\cdot}4, \ Cs^{\cdot} \ 4{\cdot}7.$$

Remy and Reisener (1927), and Baborowsky (1927), using divided cells, obtained results in the same order and with similar magnitudes. Washburn's results have also been confirmed by Taylor and Sawyer, † who used urea instead of raffinose as the reference substance. The hydration postulated by Washburn for the hydrogen ion has been definitely proved by M. Volmer's X-ray study ‡ of the monohydrate of perchloric acid, $HClO_4 . H_2O$, which is solid and polar while the acid itself is a non-polar liquid. He confirmed Hofman's idea that the hydrate is oxonium perchlorate, $H_3O^{\cdot} . ClO_4'$, having interpenetrating lattices of $H_3O^{\cdot}$ and ClO_4'. The X-ray diagram was practically identical with that of ammonium perchlorate, $NH_4^{\cdot} . ClO_4'$.

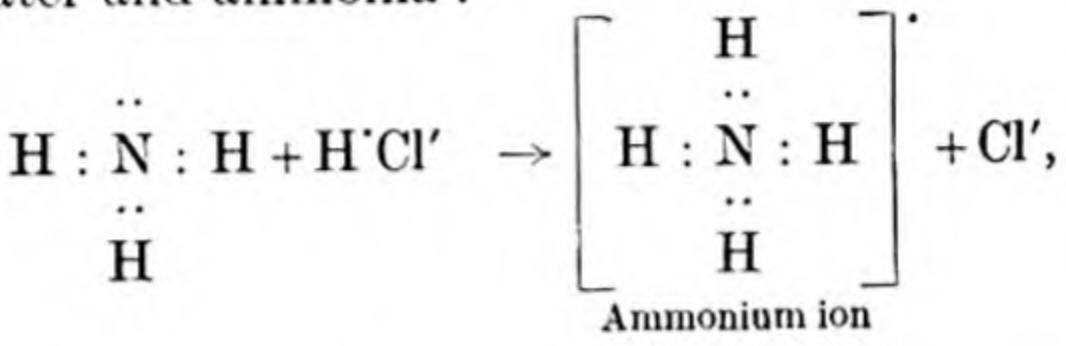
N. V. Sidgwick § has pointed out that in addition to this solvation of the ions by virtue of the dipole character of the solvent molecules, there is a definite co-ordination of the latter with the ion, and that in two ways ; either by the oxygen of a hydroxyl group acting as a donor, or by the hydrogen acting as an acceptor :

$$X \leftarrow O\begin{matrix}H\\ \\ R\end{matrix} \quad \text{or} \quad X \rightarrow H—O—R.$$

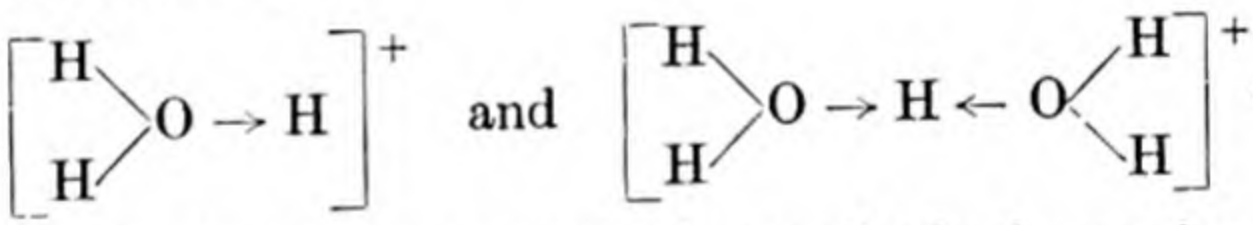
The limit of such co-ordination for either cations or anions is fixed by the covalency maximum, and the two types of grouping, co-ordinated and solvated, are for many purposes indistinguishable. This increases the difficulty of deciding the absolute magnitude of the hydration.

* *J. Amer. Ch. Soc.* **31**, 322 (1909). † *J.C.S.* 1929, 2095.
‡ *Ann.* **440**, 200 (1924). § *Electronic Theory of Valency*, 189 (1927).

The hydrogen ion is peculiar in being a simple proton, with no electrons either in the nucleus or outside it, and is pre-eminent in its mobility in hydroxylic solvents, and as an acceptor of electrons. Thus it adds readily to the lone pairs of electrons in compounds such as water and ammonia :



Sidgwick points out that the hydrogen ion can also take up two molecules of water, this representing its covalency maximum. He writes these * :



It is probable that in associated solvents the hydrogen ion cannot exist alone, and that the ionisation of acids in such solvents is directly due to their union with the hydrogen ion.

Addition to the double bond of olefines takes place in a similar way :

$$CH_2 : : CH_2 + H{\cdot}Br' \rightarrow [C_2H_4 \,.\, H]{\cdot}Br'.$$

Burton and Ingold † consider that the hydrogenation of olefines consists of a consecutive addition of two protons to the activated double bond.

Werner ‡ suggested that acids and bases are not themselves dissociated, but unite with one or other of the ions of water, an acid uniting with hydroxyl ion and a base with hydrogen ion. Each thus greatly increases the ionisation of water, giving a

* *Loc. cit.* 194.

† *J.C.S.* 1929, 2022.

‡ *Neuere Anschauungen der Anorg. Chemie*, 250 (1923).

strongly conducting solution. On neutralisation, the ions of water re-unite, leaving the ions of the salt :

$$[KOH \,.\, H^{\cdot}] + OH' + [ClH \,.\, OH'] + H^{\cdot}$$
$$= H_2O + [KOH \,.\, H^{\cdot}] + [ClH \,.\, OH'],$$

which are equivalent to hydrated metal and acid ions,

$$K^{\cdot}(H_2O) \quad \text{and} \quad Cl'(H_2O).$$

80. Electrical effects of ions. The solvation of the ions should be anticipated in the light of the electronic theory. For the charged ions will convert neighbouring molecules of the solvent into electric doublets or dipoles, which will be attracted by the ion. A group or sheath of polarised molecules will thus tend to surround the ion, moving with it and retarding it when it is urged by an external field. Such a grouping of solvent molecules around the ions must tend further to separate them, to isolate them and prevent reunion into ion-pairs, and in fact the dissociation of an electrolyte is increased by the solvation of its ions.

Apart from this effect on the solvent molecules, the ions have an important influence on each other, the chief result of which is a diminished mobility, and a consequent reduction in the so-called degree of dissociation, even of electrolytes which are completely ionised in solution. This phenomenon, known as *electrostriction*, has been discussed in various theories of strong electrolytes.

Diffusion of electrolytes into water, or into each other, occurs just as with other solutes, but owing to the differential mobilities of the ions, electrical effects are produced. In the case of hydrogen chloride solution, for example, diffusing into water, the hydrogen ions move more quickly than chlorine ions, and the water becomes positively charged while the concentrated acid assumes a negative charge. With sodium chloride solution, the sodium ion has the smaller mobility and the concentrated solution becomes positively, the water negatively charged. If the salt and acid solutions are allowed to diffuse into each other, the two effects are added, the salt solution becoming positively and the acid negatively charged. The electrostatic fields so created retard

the diffusion of the ions, and the potential gradient slowly disappears.

81. Dielectric constant. Under the influence of an external field, the molecules of a pure solvent will tend, especially in the case of polar substances, to become oriented against the field, and so to reduce its strength. This reducing effect is a measure of the dielectric constant, which is thus greater the more polar the substance. The ions of an electrolyte in such a solvent have their interionic fields reduced for a similar reason, and tend more easily to separate. The work required to separate two opposite electrical charges is inversely proportional to the dielectric constant, and thus in a medium of high dielectric constant ionisation is promoted.

The connection between the dielectric constant and the ionising power of liquids was first pointed out by J. J. Thomson in 1893 and by Nernst in 1894, and is known as the Nernst-Thomson rule: the ionising power of a solvent is greater the larger the dielectric constant. Generally, the conductance of salt solutions increases as the dielectric constant of the solvent becomes greater. Walden* showed that the concentrations of a salt at which it shows the same dissociation in two solvents are in the ratio of the cubes of the dielectric constants of the solvents:

$$\frac{C_1}{C_2} = \left(\frac{D_1}{D_2}\right)^3.$$

He found also that for electrolytic solutions, at small concentrations, the dielectric constant is less than that of the pure solvent. There is still some doubt as to the way in which the dielectric constant of electrolytic solutions varies with the concentration, and this is one of the difficulties in the completion of the Debye-Hückel theory of strong electrolytes.

Liquids with high dielectric constant, which, as stated above, is accompanied by strong ionising power, are generally associated in the liquid state.

* *Z. Phys. Chem.* **94**, 263 (1920).

The dielectric constant varies much for different liquids, as the following values show :

	D.C.		*D.C.*
Hydrogen cyanide -	96·0	Ethyl alcohol - -	26·8
Hydrogen peroxide -	93·0	Acetone - - -	26·6
Water - - -	81·0	Benzonitrile - -	25·1
Glycerol - - -	39·1	Ammonia (liq.) - -	21–23
Acetonitrile - - - -	39·0	Chloroform - -	5·2
Nitrobenzene - -	36·0	Ether - - -	4·3
Methyl alcohol - -	35·4	Benzene - - -	2·3

For any one substance the constant is not independent of temperature, but often increases rapidly as the temperature falls. This result is due to the decrease of thermal disturbance, which allows the molecules more completely to orient themselves in the electrostatic field, and is more pronounced for substances of a definite dipole character. Hydrocarbons have very low values of the constant, but these are increased by any change that confers or enhances dipole character, or by the introduction, as into benzene, of groups showing general polarity, such as the nitro- or the cyano-group.

In an investigation of the hydration of strong electrolytes, J. N. Sugden * suggested that only cations are hydrated, whilst anions depolymerise the solvent molecules. There would thus be a continuous decrease in the association of the solvent, and a consequent decrease in the dielectric constant, with increasing salt concentration. The efficiency of the depolymerisation of the solvent varies with different anions.

82. Non-aqueous solvents. Ionising power is thus a rather complex property of the solvent. It is not confined to water. Alcohols possess it to some extent, methyl alcohol acting more powerfully than ethyl alcohol. Acetone, benzonitrile, nitrobenzene, and some inorganic substances such as liquid sulphur dioxide and liquid ammonia, also give conducting solutions. On the other hand, liquids of low dielectric constant such as benzene and carbon bisulphide, ether and chloroform, are feebly ionising sol-

* *J.C.S.* **130,** 174 (1926).

vents. There is a rough proportionality between the two functions. The dielectric constant determines the force of attraction between the ions, and the force required to part them. When the dielectric constant is small, the other factors promoting ionisation become more important, and the chemical nature of the medium may then have a preponderating influence.*

83. That the reactions given by solutions of metallic salts are really those of the ions, is clearly indicated by such considerations as the following.

The reactions of calcium, for example, are the same whether the solution employed be that of the chloride, nitrate, acetate, or other salt. Further, all permanganates give similarly coloured solutions, characterised by the same absorption spectrum in solutions of equivalent concentration. The colour is that of the permanganic ion. This is true also for solutions in acetone and other organic solvents that are not readily oxidised. Again, if an alcoholic solution of silver nitrate be added to alcoholic solutions of sodium iodide and of ethyl iodide respectively, an immediate precipitate of silver iodide is obtained in the first case, but not in the second, which shows only a slow reaction. The sodium iodide is ionised to some extent in alcoholic solution : the ethyl iodide not at all. This is confirmed by the electrolytic and other properties of the solutions. In general, the conductivity and the capacity for reaction are parallel ; indeed Hittorf defined electrolytes as salts which are capable of exchanging their constituents instantaneously.

84. **Complex ions.** The nature of the ions is often difficult to decide. Thus in a solution of K_2PtCl_6 the ions are not 2K, Pt and 6Cl ; silver nitrate solution gives no precipitate of AgCl, but a yellow precipitate of Ag_2PtCl_6. The ions are thus $2K^{\cdot}$ and $PtCl_6''$, and when the salt is electrolysed, potassium separates at the cathode and $PtCl_6$ at the anode, decomposing there into Pt and 6Cl. The point can usually be decided by observing which complexes interchange themselves with others. Double salts show

* See *Chem. Soc. Ann. Reports*, 1930, 326.

the reactions of both constituents, as in the case of copper potassium sulphate, and are dissociated into the corresponding ions. Complex salts, on the other hand, like the cyanides produced by dissolving a precipitated metallic cyanide in excess of the precipitant, often dissociate in a complex way. $K_4Fe(CN)_6$ does not show any of the usual reactions for $Fe^{\cdot\cdot}$ ions ; the salt dissociates in solution into the ions $4K^{\cdot}$ and $Fe(CN)_6'' ''$. So also $KAg(CN)_2$ dissociates into $K^{\cdot}$ and $Ag(CN)_2'$. It was suggested by Glasstone * that ions such as $(Ag_2CN)^{\cdot}$ and $(Ag_3CN)^{\cdot\cdot}$ may exist in solution, formed thus :

$$Ag(CN)_2' \rightleftharpoons Ag^{\cdot} + 2CN',$$
$$2Ag^{\cdot} + CN' \rightleftharpoons (Ag_2CN)^{\cdot},$$

so that at the cathode

$$(Ag_2CN)^{\cdot} \rightarrow Ag^{\cdot} + CN' + Ag(\text{pptd.}) + \oplus$$

Reychler showed (1914) that in ammoniacal solutions of copper sulphate and of silver chloride, four molecules of ammonia are transported for each $Cu^{\cdot\cdot}$ ion deposited on the cathode, and two for each $Ag^{\cdot}$ ion; that is, the ions $[Cu(NH_3)_4]^{\cdot\cdot}$ and $[Ag(NH_3)_2]^{\cdot}$ are transported as such. He found earlier that 2 molecules NH_3 added to 1 molecule $AgNO_3$ in solution did not alter the freezing point of the solution, that is, the number of dissolved molecules (or ions) was not changed.

85. Acids and bases. The characteristic reactions of acids and bases are due to the ions of $H^{\cdot}$ and OH' respectively which their solutions contain. Strong acids or bases, that is, those which exhibit these properties in the most marked manner, are those which dissociate to the greatest degree. Ostwald compared the relative strengths of acids by comparing the influence exerted by them, in equivalent quantities, on such reactions as the hydrolysis of methyl acetate, the inversion of cane sugar, the conversion of acetamide into ammonium acetate, reactions all of which are catalysed by the presence of $H^{\cdot}$ ions. His results showed a close agreement in the order of strength of acids deduced from these various methods, and agreed also with that given by conductance measurements.

* *J.C.S.* **132**, 690 (1929).

The hydrogen ion is now regarded not as a free proton, but as solvated with a molecule of water in the form of the oxonium ion $H_3O^{\cdot}$. The ionisation of hydrogen chloride in solution is regarded as

$$HCl + H_2O \rightleftharpoons H_3O^{\cdot} + Cl' \quad \text{and not} \quad HCl \rightleftharpoons H^{\cdot} + Cl',$$

and in alcohol $HCl + ROH \rightleftharpoons ROH_2^{\cdot} + Cl'$.

A more general conception of acidity and basicity was suggested independently by Lowry * and by Brönsted in 1923. An acid is regarded as a substance which can split off a proton—a proton-donor, and a base as a proton-acceptor—a substance which can take up a proton to form an acid :

$$\underset{\text{Acid}}{A} \rightleftharpoons H^{\cdot} + \underset{\text{Base}}{B}.$$

In this sense water acts as a feeble base, uniting with a proton to form the oxonium ion, and so also do the anions of weak acids like acetic whose ionisation is reversible :

$$CH_3COOH \rightleftharpoons CH_3COO' + H^{\cdot}.$$

But strong acids, on the other hand, are practically completely and irreversibly ionised in solution, and the anion does not act as a base. The chloride ion Cl', for example, is a much weaker base than water, and has practically no catalytic action. This conception of the nature of acids and bases has been supported by experimental work by Brönsted and others.†

Polybasic acids usually show different dissociation constants for the separate $H^{\cdot}$ ions. Instead of the complete dissociation in one reaction :

$$H_2A \rightleftharpoons 2H^{\cdot} + A'' ;$$

such acids commonly dissociate according to the scheme :

$$H_2A \rightleftharpoons H^{\cdot} + HA', \quad \text{then} \quad HA' \rightleftharpoons H^{\cdot} + A''.$$

The anion HA' behaves as a weak acid, and in the view of Lowry and of Brönsted, is also a base since it is a proton-acceptor.‡

* *Chem. and Industry*, **42**, 43 (1923).

† See Kilpatrick and Kilpatrick, *Chem. Reviews*, **10**, 213 (1932).

‡ Niels Bjerrum, *ibid.*, **16**, 287 (1935). W. F. Luder, *ibid.*, **27**, 547 (1940).

Dissociation in stages also occurs with the salts of polybasic acids, and with polyacid bases and their salts.

When the second or subsequent dissociation constant of a polybasic acid or a polyacid base is very small, an n basic acid may behave as $(n-1)$ or $(n-2)$ basic, even in dilute solution. Thus phosphoric acid, H_3PO_4, which is tribasic, yields the disodium salt, Na_2HPO_4, on neutralisation with sodium hydroxide solution.

86. Hydrogen ion concentration. In this sense the acidity of any solution is due to the $H^{\cdot}$ ions actually present, and must be clearly distinguished from the total amount of ionisable hydrogen, which is estimated by the ordinary chemical methods of acidimetry. Thus, while equivalent amounts of hydrochloric acid and of acetic acid require the same quantity of sodium hydroxide for neutralisation, the catalytic methods above indicated, or the conductivities, show that the hydrochloric acid is ionised to a much greater degree than the acetic. For 0·001 N solutions the proportions are 99 per cent. and 13·6 per cent. respectively. In the case of the weak acetic acid, titration with alkali removes the free $H^{\cdot}$ ions, thus displacing the equilibrium; more acid at once ionises, and the reaction proceeds so to the end point.

Conductance measurements provide the most accurate method for determining hydrion concentration.

Water itself is very slightly dissociated, the ions being of course present in exactly equivalent amounts. From conductance measurements of the purest water obtainable by vacuum distillation, Kohlrausch * found the concentration to be, in gram-ions per litre,

$$[H^{\cdot}] = [OH'] = 0{\cdot}88 \times 10^{-7} \text{ at } 18°,$$

or

$$1{\cdot}05 \times 10^{-7} \text{ at } 25°,$$

or about 1 gram $H^{\cdot}$ ions and 17 grams OH' ions in 10 million litres.

This is true also for all neutral aqueous solutions. And in any aqueous solution, since the concentration of undissociated water

* *Wied. Ann.* **53**, 209 (1894); *Z. phys. Chem.* **14**, 317 (1894).

molecules is constant, it must follow in accordance with the law of mass action

$$H_2O \rightleftharpoons H^{\cdot} + OH'$$

that the product of the ion-concentrations is also constant :

$$[H^{\cdot}] \times [OH'] = 1 \times 10^{-14 \cdot 14}.$$

The temperature-coefficient of ionisation of pure water is much higher (5·8 per cent. at 18°) than that for most electrolytes (2–2·5 per cent.) or for ordinary distilled water (2 per cent.).

As these $H^{\cdot}$ ion concentrations are so very small, Sörensen in 1909 expressed them in the logarithmic form, with change of sign, using for this the symbol *p*H. Thus a decinormal solution of hydrochloric acid, assuming it to be fully dissociated, would have a $H^{\cdot}$ ion concentration of $N \times 10^{-1}$ or *p*H1. Since the dissociation is only about 97 per cent., the actual value is *p*H1·01. In pure water, we have the values *p*H 7·07 and *p*OH 7·07. The greater the *p*H value, of course, the lower is the actual concentration of $H^{\cdot}$ ions. There is further no need to determine the *p*OH value, since the sum of the two must always be 14·14.

Further reference will be made to this in the remarks on indicators.

87. The action of metals on acids. The chemical activity of an element is dependent on the number of electrons in the outer shells of its atoms. The number of these electrons determines the valency of the element, and the readiness with which the atoms part with them is a measure of the chemical activity.

When a metal is placed in a solution containing hydrogen ions, its atoms show a tendency to part with these electrons and become ions. When zinc, for example, is placed in dilute sulphuric acid, each atom of the metal dissolved loses two electrons, which are taken up by two hydrogen ions. The latter thus become atoms and form molecules of hydrogen which is evolved as gas. The atoms of zinc dissolved thus become bivalent cations :

$$Zn + 2H^{\cdot} + SO_4'' = Zn^{\cdot\cdot} + SO_4'' + H_2.$$

The elements can be arranged in an electrical series such that the

ions of hydrogen, which occupies the zero position, give up their positive charges to any element above hydrogen in the series: Cs, Rb, K, Na, Li, Ba, Sr, Ca, Mg, Al, Zn, Fe, Pb, Sn, H (zero), Bi, Cu, Ag, Hg, Pt, Au.

The first five elements in this series, the alkali metals, readily attack cold water, passing into ions which become associated with the OH′ ions in the system, forming soluble hydroxides and liberating hydrogen:

$$2K + 2H^{\cdot} + 2OH' \rightarrow 2K^{\cdot} + 2OH' + H_2.$$

Hydroxides of barium, strontium and calcium are progressively less soluble and the metals have a diminishing action on water. Magnesium hydroxide is very sparingly soluble, and forms a protective coating on the metal, which thus has little action on cold water, though this increases on heating. When magnesium is boiled in water, the liquid soon becomes alkaline.

The presence of carbon dioxide in water increases the concentration of hydrogen ions and so accelerates these changes. But in presence of atmospheric oxygen it also results in the formation of basic carbonates, which, being generally insoluble, may protect the metal and check the action, as in the case of lead (p. 139).

In dilute acids the concentration of hydrogen ions is greater still, and hydrogen is readily evolved by the action of dilute hydrochloric or sulphuric acid on magnesium, zinc or iron. Pure metals, as a rule, react very slowly; the impurities commonly present, such as iron, etc., in zinc, set up galvanic action on the exposed surface and thus accelerate the liberation of hydrogen. A similar result is attained by the addition of a little platinic chloride or copper sulphate solution to the pure zinc, or of mercuric chloride to aluminium; the Zn/Pt or Zn/Cu couple, or the Al/Hg couple thus produced are useful reducing agents even in water. The position of a metal in the electrochemical series may be much influenced by the presence of impurities.

Very dilute nitric acid slowly evolves hydrogen when placed in contact with magnesium. The stable NO_3' ions are not reduced under these conditions. But greater concentrations of the acid contain molecules of HNO_3 in addition to its ions, and these are

reduced by the nascent hydrogen, forming oxides of nitrogen or even ammonia. The extent of the reduction depends on concentration, temperature, and the solubility of the nitrate formed.

Copper, silver and mercury do not liberate hydrogen from dilute sulphuric or hydrochloric acids. Their position in the electrochemical series explains this. On the contrary, hydrogen, especially under pressure, precipitates these and other metals, including nickel and cobalt, from solutions of their salts. A certain temperature is required before the reaction begins.* Iron and zinc, being more electropositive, are not precipitated in this way.

Copper dissolves slowly in dilute sulphuric acid in presence of air, forming copper sulphate ; or in hot concentrated sulphuric acid liberating sulphur dioxide ; or in nitric acid, especially in presence of nitrous acid, forming various oxides of nitrogen according to the concentration of the acid and the temperature : in each case the first reaction is the oxidation of the copper.

88. Hydrolysis of salts. The hydrolytic action of water on certain salts is due to the ionisation of the water itself. In the case of a salt made from a weak acid, like sodium acetate, there are in solution the systems

$$NaC_2H_3O_2 \rightleftharpoons Na^{\cdot} + C_2H_3O_2'$$

and

$$2H_2O \rightleftharpoons H_3O^{\cdot} + OH',$$

with possibility of interchange among the ions. Since acetic acid is only feebly dissociated, the $C_2H_3O_2'$ ions remove $H^{\cdot}$ ions from the system to form undissociated molecules of acetic acid, while there is no corresponding removal of OH' ions, NaOH being a strong base largely dissociated. The result is a reduction of the hydrion concentration, a preponderance of OH' ions, and an alkaline reaction. It may be calculated from the catalytic effect on the hydrolysis of ethyl acetate, that in a decinormal solution, sodium acetate is hydrolysed to the extent of 0·008 per cent., and sodium cyanide to 1·10 per cent. That this hydrolysis increases on dilution, as the theory requires, may be illustrated very simply by Rose's experiment. A concen-

* Ipatiev, *Ber.*, **42**, 2078 (1909).

trated solution of borax is coloured blue with litmus, and acetic acid is added until the litmus just turns red. On addition of water the litmus again turns blue, owing to the increased hydrolysis.

Conversely all salts formed by the union of strong acids with weak bases, like ferric chloride or copper sulphate, are slightly hydrolysed in aqueous solution and have a distinct acid reaction. Basic salts often separate on standing.

When both the acid and the base are weak, but soluble, the salt is very largely decomposed in water. If the acid and the base are not only weak but one at least sparingly soluble, the salt practically will not exist in water. Thus, for example, aluminium carbonate or sulphide are not formed by precipitation, and if the sulphide prepared in the dry way be placed in water, it decomposes into the hydroxide and sulphuretted hydrogen. So also silver borate, which separates as a white precipitate on mixing a concentrated solution of borax with silver nitrate, in dilute solution is decomposed, giving a brown precipitate of silver oxide. Aluminium and chromium acetates, again, are hydrolysed on boiling their aqueous solutions, giving deposits of the hydroxides (mordants), and zinc, iron, copper, aluminium and other metals give basic carbonates.

89. The solubility-product. When a solution is saturated, the dissolved substance is in equilibrium with the solid phase, and the concentration law is applicable. For illustration, take the case of lead sulphate :

$$PbSO_4 \text{ (solid)} \rightleftharpoons PbSO_4 \text{ (dissolved)} ;$$

let the concentrations at a given temperature be expressed as :

$$[\text{solid}] \quad [\text{dissolved subs.}],$$

then we have the relationship

$$\frac{[\text{dissolved subs.}]}{[\text{solid}]} = k \text{ (constant)}.$$

Since the active mass of a substance in the solid phase is constant, the concentration in the solution also must be constant for any given temperature. This is in accord with our knowledge of solubility.

In the case of salts and other ionisable substances, the dissolved portion exists partly as ions, and the equilibrium law controls this reaction also, so that we have the system :

$$PbSO_4(\text{dissolved}) \rightleftharpoons Pb^{\cdot\cdot} + SO_4'',$$

and for the ionisation equilibrium

$$\frac{[Pb^{\cdot\cdot}][SO_4'']}{[\text{dissolved subs.}]} = k' \text{ (constant).}$$

Multiplying these two equations, we find

$$\frac{[Pb^{\cdot\cdot}][SO_4'']}{[\text{solid}]} = kk' ;$$

and since the concentration of the solid phase is constant it follows that

$$[Pb^{\cdot\cdot}][SO_4''] = K \text{ (constant).}$$

This product of the ion-concentrations is called the solubility-product, or ion-product, and is constant in all cases when the solution is saturated, or in equilibrium, with the solid. This was first pointed out by van't Hoff (1889). The rule is independent of any assumption as to the constitution of the undissociated substance, or of the balance between the latter and its ions, which in the case of strong electrolytes is not in strict agreement with the equilibrium law.

In the general case of a substance dissociating into several ions,

$$M_mB_n \rightleftharpoons mM^{\cdot} + nB',$$

the solubility-product is of the form

$$[M^{\cdot}]^m[B']^n = K \text{ (constant).}$$

It is thus, for any given temperature, the product of the ion-concentrations, each raised to the power indicated by the number of ions of that kind produced from one molecule of the salt.

90. Precipitation. These considerations are of special interest in reference to the precipitation of sparingly soluble substances. Normally the liquid is saturated with the substance precipitated. If the concentration in the liquid phase is such that the ion-product

is less than the normal value corresponding with the temperature, the liquid will exert a solvent action on the precipitate. If, on the other hand, the solubility-product is exceeded, the liquid is supersaturated.

It has long been known that the addition of an excess of the precipitant renders the precipitate less soluble, temperature and other conditions being equal, and this device is commonly practised in analysis. The explanation is the general one, that the presence of a second electrolyte having one ion in common with the first, reduces the solubility of the first.* For this addition will obviously increase the concentration of the common ion, say the $[SO_4'']$ in precipitating lead sulphate with a slight excess of sulphuric acid. But the solubility-product $[Pb^{\cdot\cdot}][SO_4'']$ remains constant, so that $[Pb^{\cdot\cdot}]$ must diminish. In other words, some of the ionised substance passes to the solid phase, and the precipitation is rendered more complete. The same reason underlies the practice of washing precipitates with a dilute solution of a substance having one ion in common with the precipitate, as mercurous chromate with mercurous nitrate, magnesium ammonium phosphate with ammonia, or ammonium phosphomolybdate with ammonium nitrate.

91. Salting-out. Changes of solubility may be effected by changing the composition of the solvent, as by the addition of alcohol in the precipitation of lead sulphate or strontium sulphate, or in the process of salting-out so frequently used in organic work. Thus alcohol or ether may be separated from water by dissolving potassium carbonate in the mixture ; soap is separated from its aqueous solution by addition of common salt. Such actions are due to quite other reasons than the diminution of solubility in the presence of a common ion, explained under the previous heading ; there is no relationship of this kind. The ions of the added salt polarise and attract the solvent and other molecules present, especially the readily polarisable molecules of water, with which they form solvates (79). This results in the formation of a con-

* Nernst, *Z. phys. Chem.* **4**, 372 (1889). A. A. Noyes, *ibid.* **6**, 241 (1890) ; **9**, 603 (1892) ; **26**, 152 (1898).

centrated aqueous solution of the added salt, from which the original solute is excluded and precipitated. The nature of the latter has little influence on the process.

92. **The redissolving of precipitates**, in most cases, may be explained in terms of the solubility product. Thus zinc hydroxide dissolves in either hydrochloric acid or sodium hydroxide. In the former case, it shows basic properties and in the latter, acidic. Such an amphoteric electrolyte may be called an *ampholyte*. To function as a base it must liberate OH' ions, and as an acid, $H^{\cdot}$ ions, with the equivalent amounts respectively of $Zn^{\cdot\cdot}$ and ZnO_2'' ions. The addition of an acid to the substance will remove OH' ions, and further ionisation of zinc hydroxide into $Zn^{\cdot\cdot}$ and $2OH'$ will result until the hydroxide is completely dissolved :

$$\underset{\text{solid}}{Zn(OH)_2} \rightarrow \underset{\text{solution}}{Zn(OH)_2} \rightarrow Zn^{\cdot\cdot} + 2OH'.$$

In presence of a base, on the other hand, $H^{\cdot}$ ions will be removed, and the zinc hydroxide will ionise in the other sense, thus acting as an acid :

$$\underset{\text{solid}}{Zn(OH)_2} \rightarrow \underset{\text{solution}}{Zn(OH)_2} \rightarrow 2H^{\cdot} + ZnO_2''.$$

In the first case zinc salts are formed, and in the second, alkali zincates such as Na_2ZnO_2.

Similar considerations apply to the action of strong acids on sparingly soluble salts of weak (feebly dissociated) acids, such as calcium phosphate or ferric benzoate.

Magnesium hydroxide, to take another example, dissolves in ammonium salts, and if these be added in advance, no precipitate is obtained on addition of ammonium hydroxide. This used to be attributed to the formation of double salts, as $MgCl_2 . NH_4Cl$. Such salts do exist, but similar double salts are formed with KCl and NaCl, yet these do not prevent precipitation with ammonia. The true explanation is found in the interactions of the ions. We have

$$\underset{\text{(solid)}}{Mg(OH)_2} \rightleftharpoons \underset{\text{(dissolved)}}{Mg(OH)_2} \rightleftharpoons Mg^{\cdot\cdot} + 2OH'$$

$$2NH_4Cl \rightleftharpoons 2Cl' + 2\overset{+}{N}H_4^{\cdot}$$

$$\Downarrow$$

$$2NH_4OH.$$

The addition of NH_4Cl, which is strongly ionised, causes a large increase in the concentration of $NH_4^{\cdot}$ ions. This diminishes the total concentration of OH′ ions, since NH_4OH is a weak base and only slightly ionised. To maintain the equilibrium of the $Mg(OH)_2$ system, therefore, $Mg(OH)_2$ must pass from the solid phase to the liquid, and this continues so long as the product $[Mg^{\cdot\cdot}][OH']^2$ is less than the solubility product for magnesium hydroxide.

For this reason also magnesium salts are only partially decomposed by ammonium hydroxide : some ammonium salt is always formed and acts in the manner just described. Further, an excess of the ammonium salt added beforehand so reduces the ionisation of the NH_4OH that the product $[Mg^{\cdot\cdot}][OH']^2$ never reaches the value of the solubility product. Consequently no precipitate is produced.

Excess of the precipitant often exerts a solvent action on the precipitate. Thus when ammonia is added to salts of copper, nickel, etc., the hydroxide first formed dissolves in excess of ammonia to yield compound ions of the form $M(NH_3)_n$. The corresponding salts are readily soluble, and are again decomposed on addition of acid, the $(NH_3)_n$ forming $NH_4^{\cdot}$ ions with the $H^{\cdot}$ ions of the acid, and the metallic hydroxide is again precipitated as the neutral point is approached.

Complex ions are also produced when the alkali cyanides dissolve the cyanides or hydroxides of the heavy metals. Frequent reference has already been made to these.

SYSTEMATIC DETECTION OF THE IONS.

93. The detection of cations in a mixture containing several is facilitated by a preliminary separation into groups. These groups depend chiefly on similarities in the solubility of certain compounds of the metals, and therefore vary slightly according to the compounds chosen for precipitation. They do not generally follow the natural classification of the elements ; but in some cases, such as barium, strontium and calcium, the family resemblance is so strong as to bring these metals into the same analytical group also.

The reactions upon which such separations are based are given in Section II., and a method of analysis follows these. It will readily be understood that this is not the only method available : some alternatives are suggested, and others will occur to the student in practice. The following observations are of special interest in regard to the separation of the metals into groups.

The advantage of a slight excess of precipitant has been explained in par. 90. In the **lead group** this is rendered necessary by the fact that lead chloride is appreciably soluble in cold water. A small excess of dilute hydrochloric acid, however, so reduces the concentration of $Pb^{\cdot\cdot}$ ions, that with care lead may be almost completely precipitated in group I., and mere traces should pass over to the second group. The most effective concentration of hydrochloric acid for this purpose is about 100 g. HCl per litre at 20° (say 3N). Most chlorides also diminish the solubility of $PbCl_2$. Mercuric chloride causes a slight increase. Ammonium chloride forms complex salts, from some of which it is difficult to remove the lead as sulphate.

It should be remembered also that lead chloride is soluble in concentrated hydrochloric acid, owing to the formation of complexes such as Berthelot's hydrochloroplumbous acid, H_2PbCl_4 ; this is decomposed by water, and thus $PbCl_2$ is precipitated on diluting. Mercurous chloride also may be converted in presence of oxidising agents (e.g. nitric acid or nitrates) into the soluble mercuric salt.

The copper group comprises the cations whose sulphides are insoluble in dilute hydrochloric acid. The concentration of the acid at this point is of great importance, and should in no case exceed 0·5 N.

Precipitation with sulphuretted hydrogen must be made with great care. In a solution saturated with the gas at 15° there is only 0·47 gram per 100 c.c. Hydrosulphides are not present to any extent in the precipitation of sulphides ; the S'' ion is the effective precipitant. But the gas in solution is very feebly ionised :

$$H_2S \rightleftharpoons 2H^{\cdot} + S'',$$

and

$$[H^{\cdot}]^2 \times [S''] = k,$$

and thus the sulphides are more or less sensitive to the action of concentrated acids, that of cadmium being the most easily dissolved. Addition of acid increases the concentration of $H^{\cdot}$ ions, thereby reducing that of the S'' ions ; and when this is so small that the product $[Cd^{\cdot\cdot}] \times [S'']$ is less than the solubility product for CdS, the sulphide dissolves.

Care must therefore be taken to avoid undue excess of acid, and to test the filtrate by diluting with water to reduce the concentration of $H^{\cdot}$ ions, and again saturating with H_2S. If no further precipitate is obtained the conditions were right at the outset.

CuS is very sparingly soluble in $(NH_4)_2S$, and HgS in K_2S or Na_2S, forming the salt K_2HgS_2 with the complex ion HgS_2''. Therefore if mercury and tin are absent, it is better to use sodium hydroxide to dissolve the sulphides of As, Sb and Sn.

The increase in electropositive character with increasing atomic weight of the metals As, Sb, Bi (periodic group Vb) is well illustrated in the behaviour of the sulphides. As_2S_3 decomposes ammonium carbonate, in which Sb_2S_3 and Bi_2S_3 are insoluble. Bi_2S_3 is unaffected even by $(NH_4)_2S$, in which As_2S_3 is easily, and Sb_2S_3 sparingly soluble. Sb_2S_3 is more readily dissolved by *yellow* ammonium polysulphides, which convert the metallic sulphides into the higher, more acidic sulphides :

$$Sb_2S_3 + 3(NH_4)_2S + S_2 \rightarrow 2(NH_4)_3SbS_4,$$
$$SnS + (NH_4)_2S_2 \rightarrow (NH_4)_2SnS_3.$$

Arsenic sulphides are not precipitated from solutions of alkali arsenites or arsenates in the absence of acid. This is referred to in the section on colloids (97).

Antimony and bismuth readily form oxy-salts on addition of water to the normal salts or their solutions in acids. Since these oxy-salts, however, are converted into sulphides by the action of hydrogen sulphide :

$$2SbOCl + 3H_2S \rightleftharpoons Sb_2S_3 + 2HCl + 2H_2O,$$

the addition of more acid is unnecessary. N . HCl is of sufficient concentration to prevent the formation of oxy-salts.

The aluminium group contains the cations whose hydroxides are insoluble in ammonia and ammonium salts, namely $Fe^{\cdot\cdot\cdot}$,

$Cr^{...}$ and $Al^{...}$. These may be separated in this way from the metals of the zinc group, whose hydroxides are not precipitated by NH_4OH in presence of ammonium salts. But the method is occasionally inaccurate, inasmuch as the hydroxides of $Al^{...}$, $Cr^{...}$ and $Zn^{..}$ tend to unite with the basic hydroxides of the zinc group, which may thus be lost. An alternative method is to precipitate the two groups together with H_2S in presence of NH_4OH and NH_4Cl. The precipitate then contains the hydroxides of aluminium and chromium and the sulphides of iron and the zinc group. These may be dissolved in HCl and separated in various ways. A quantitative method is found in the action of suspended barium carbonate on the chlorides. This substance is not sufficiently soluble to precipitate the carbonates of the zinc group, but it precipitates the hydroxides of the aluminium group, which are thus completely separated from the solution of the zinc group chlorides.

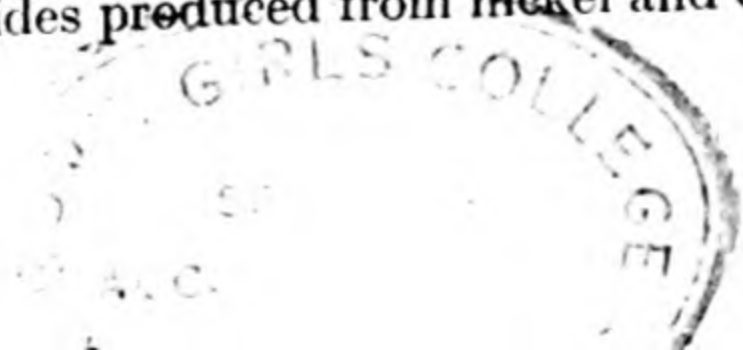
$$2FeCl_3 + 3BaCO_3 + 3H_2O = 2Fe(OH)_3 + 3BaCl_2 + 3CO_2.$$

Iron salts, if present, should therefore be oxidised before the addition of barium carbonate.

Manganese is so easily oxidised in alkaline or slightly acid solutions that it is very difficult to prevent its precipitation with the aluminium group in presence of ammonia. Even in the barium carbonate method, prolonged exposure to the air may cause the formation of $Mn(OH)_3$, which will then separate with the other tervalent hydroxides.

The zinc group sulphides are only partially precipitated from a neutral solution. As was noted above in the case of cadmium, sulphuretted hydrogen is so slightly ionised in solution that the concentration of S″ ions is too small to raise the product of the ion-concentrations, say $[Zn^{..}]\,[S'']$, to the value of the solubility-product for that substance. But when a little alkali or alkali sulphide is added, this alkali sulphide is strongly ionised and the necessary concentration of S″ ions is at once attained: the precipitation of zinc sulphide is then rapid and complete.

The sulphides produced from nickel and cobalt salts in absence



of air are $Ni(SH)_2$, $Co(SH)_2$ and $Co(SH)_3$;* these dissolve in acid with liberation of H_2S, but become gradually less soluble on standing. When dried in nitrogen they form the corresponding sulphides. In air, oxidation takes place and sulphates may be formed.

The barium group cations are easily detected and distinguished by their flame colorations, which should be examined by means of the spectroscope. The metals form a number of sparingly soluble salts, the solubility of each varying with the atomic weights of the metals. Some of these are shown in the following table,† in grams per litre at 18–20° :

	Barium	Strontium	Calcium
Hydroxide - -	37·0	7·7	1·7
Carbonate - -	0·018	0·0066	0·011
Sulphate - -	0·0023	0·114	2·023
Chromate - -	0·0035	1·2	4·0
Oxalate - - -	0·0905	0·046	0·0055

From these numbers it appears that the carbonates have the most uniformly small solubility, and accordingly ammonium carbonate is used as the group reagent. But barium carbonate is comparatively easily soluble, and an excess of the reagent and the lapse of a little time are required to ensure complete precipitation.

The metals of this group afford a good example of fractional precipitation. Thus if ammonium carbonate be added in small quantities to a solution containing salts of all three metals, the strontium is first precipitated to the exclusion of the others : and similarly calcium before barium. This may easily be proved by experiment. Again, if the three sulphates are boiled with sodium carbonate solution, the barium sulphate is so slowly attacked that it may be separated from the strontium and calcium, these being converted into carbonates which may be dissolved in acetic acid.

Magnesium is not precipitated by ammonium hydroxide or carbonate in presence of ammonium salts, as explained in par. 92,

* Middleton and Ward, *J. Chem. Soc.*, **147**, 1459 (1935).

† Various Authorities. See Comey's *Dictionary of Chemical Solubilities* (Macmillan and Co. Ltd.).

and may be detected in the filtrate from the barium group by the addition of sodium or ammonium phosphate. It should be remembered that any small quantities of other metals, as for instance barium, which have been passed over from other groups, will be precipitated here, since most phosphates are insoluble in ammonia.

OXIDATION AND REDUCTION

94. Oxidation, in its original sense, meant the addition of oxygen to a system. The term has now a much wider signification and is applied to systems from which oxygen may be entirely absent. It may be defined as the change in the valency of an atom which results from the loss of one or more electrons. The acceptor of those electrons is said to be reduced, and reduction is defined generally as the change in valency caused by the acquisition of electrons. Oxidation thus involves an increase in positive valency, and reduction an increase in negative valency.

When a ferrous salt is oxidised, the change to the ferric salt is equivalent to the oxidation of ferrous to ferric oxide :

$$2FeO + \tfrac{1}{2}O_2 \rightarrow Fe_2O_3,$$

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O,$$

$$2FeCl_2 + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2FeCl_3 + H_2O.$$

In solutions of salts, the oxygen does not actually combine with the metal, and it need not even be present, for the same change may be effected by means of chlorine :

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3,$$

$$6FeSO_4 + 3Cl_2 \rightarrow 2FeCl_3 + 2Fe_2(SO_4)_3.$$

Expressed in terms of the ions, the important change is an increase in the valency of the cation. Thus by the loss of an electron, a ferrous ion is oxidised to a ferric ion :

$$Fe^{\cdot\cdot} - \epsilon \rightarrow Fe^{\cdot\cdot\cdot},$$

and the electron lost by the ferrous ion is taken up either by the hydrogen ion of an acid to form water if oxygen is present :

$$2[Fe^{\cdot\cdot} + 2Cl' + H^{\cdot} + Cl'] + \tfrac{1}{2}O_2 \rightarrow 2[Fe^{\cdot\cdot\cdot} + 3Cl'] + H_2O$$

or by the chlorine atom to form chloride ion :

$$2Fe^{\cdot\cdot} + 4Cl' + Cl_2 \rightarrow 2Fe^{\cdot\cdot\cdot} + 6Cl'.$$

The reverse process represents a reduction : ferric ion takes up one electron in passing to the ferrous ion :

$$Fe^{\cdot\cdot\cdot} + \epsilon \rightarrow Fe^{\cdot\cdot}.$$

When ferric chloride, for example, is used for the volumetric estimation of tin (542), we say that the iron is reduced while the tin is oxidised :

$$SnCl_2 + 2FeCl_3 \rightarrow SnCl_4 + 2FeCl_2,$$

or

$$Sn^{\cdot\cdot} + 2Fe^{\cdot\cdot\cdot} \rightarrow Sn^{\cdot\cdot\cdot\cdot} + 2Fe^{\cdot\cdot},$$

each stannous ion loses two electrons, thereby forming the tetravalent stannic cation ; each ferric ion gains one electron, forming the ferrous ion, and the valency is simultaneously diminished from three to two. The chloride ions have no influence on the reaction : they suffer no change of valency or of number.

Oxidation of an anion is accompanied by a decrease in its (negative) valency. When ferrocyanide, for example, is oxidised to ferricyanide, each anion loses one electron, which serves to produce either hydroxide ion (from a peroxide), chloride ion (from chlorine), or cerous cation (from ceric cation) :

$$\xrightarrow{H_2O_2} Fe(CN)_6''' + OH'$$

$$Fe(CN)_6'''' \xrightarrow[Cl_2]{} \quad ,, \quad + Cl'$$

$$\xrightarrow{Ce^{\cdot\cdot\cdot\cdot}} \quad ,, \quad + Ce^{\cdot\cdot\cdot}.$$

The potassium or other cations are unchanged in number or valency and need not be considered.

Reduction is the converse of any of the above aspects of oxidation. It is the result of acquiring electrons, and involves the loss of a positive charge.* An oxidising agent is thus a substance which takes away or receives electrons from another substance. A reducing agent is a substance which gives electrons to another.

In all oxidation-reduction changes the sum of the electric

* See also Glasstone, *Oxidation-reduction potentials*. Inst. Chem. Lecture, 1937.

charges must be the same before and after the reaction. In the case of permanganate, the anion MnO_4' is the oxidising agent, and the manganese atom has a positive valency of seven. In changing to the manganous ion $Mn^{\cdot\cdot}$, each manganese atom therefore gains five electrons, and is capable of oxidising five atoms of ferrous iron. Hence, in presence of hydrion (acid) sufficient to take up these electrons and form water with the oxygen, we have

$$MnO_4' + 5Fe^{\cdot\cdot} + 8H^{\cdot} \rightarrow Mn^{\cdot\cdot} + 5Fe^{\cdot\cdot\cdot} + 4H_2O.$$

The potassium or other cations of the permanganate, and the anions of the acid, remain as such and have no bearing on the reaction. By inserting these, however, we get an equation of the ordinary type :

$$KMnO_4 + 5FeCl_2 + 8HCl \rightarrow MnCl_2 + 5FeCl_3 + KCl + 4H_2O.$$

When dichromate is used as an oxidising agent, the divalent anion Cr_2O_7'' is converted into tervalent chromium cation $Cr^{\cdot\cdot\cdot}$: each chromium atom gains three electrons, while each ferrous ion loses one. One molecule of dichromate will therefore oxidise six molecules of a ferrous salt, and the oxygen atoms are taken up by hydrogen ions from an acid to form water :

$$Cr_2O_7'' + 6Fe^{\cdot\cdot} + 14H^{\cdot} \rightarrow 2Cr^{\cdot\cdot\cdot} + 6Fe^{\cdot\cdot\cdot} + 7H_2O.$$

The potassium ions of the dichromate, and the chloride or sulphate ions of the iron salt and the acid, have no part in the reaction, but as in the last case they may be expressed in the total equation of material :

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O.$$

Among carbon compounds similarly the balance of electric charges must always be maintained. When an alcohol is oxidised to the aldehyde, the aldehyde carbon has lost two electrons. Since the chromium atoms in the anion Cr_2O_7'' gain a total of six electrons, it is clear that one molecule of dichromate will oxidise three molecules of alcohol :

$$Cr_2O_7'' + 3CH_3CH_2OH + 8H^{\cdot} \rightarrow 2Cr^{\cdot\cdot\cdot} + 3CH_3CHO + 7H_2O.$$

An equation expressing the total change of substance may be written as before.

Ceric sulphate is a useful oxidising agent. It may be readily reduced to cerous sulphate, each atom of the metal gaining one electron :

$$2Ce(SO_4)_2 + 2FeSO_4 \rightarrow Ce_2(SO_4)_3 + Fe_2(SO_4)_3,$$

or

$$2Ce^{\cdots\cdot} + 2Fe^{\cdot\cdot} \rightarrow 2Ce^{\cdot\cdot\cdot} + 2Fe^{\cdot\cdot\cdot}.$$

Among the more common reducing agents, ferrous salts take an important place, and in this sense act more powerfully in alkaline than in acid media, partly because the very small solubility product of ferric hydroxide causes its complete removal from the system :

$$2Fe^{\cdot\cdot} + 4OH' + O + H_2O \rightarrow 2Fe(OH)_3.$$

Sulphur dioxide unites directly with oxygen to form the trioxide :

$$S^{\cdots\cdot} - 2\epsilon \rightarrow S^{\cdots\cdots},$$

and is therefore a reducing agent in the form of either sulphurous acid or the sulphites.

Stannous ion forms stannic ion by the loss of two electrons, as in the reduction of ferric or mercuric chlorides :

$$Sn^{\cdot\cdot} + 2Fe^{\cdot\cdot\cdot} \rightarrow Sn^{\cdots\cdot} + 2Fe^{\cdot\cdot},$$

$$Sn^{\cdot\cdot} + 2Hg^{\cdot\cdot} \rightarrow Sn^{\cdots\cdot} + 2Hg^{\cdot},$$

while the stannite anion SnO_2'' similarly changes to stannate anion, SnO_3'', by the loss of two electrons from the tin atom accompanied by the direct addition of one atom of oxygen :

$$SnO_2'' + Bi_2O_3 \rightarrow SnO_3'' + 2BiO.$$

Titanous chloride, $TiCl_3$, is applied in many reactions as a reducing agent,* as it passes easily into the stable tetrachloride :

$$TiCl_3 + FeCl_3 \rightarrow TiCl_4 + FeCl_2,$$

or

$$Ti^{\cdots} + Fe^{\cdot\cdot\cdot} \rightarrow Ti^{\cdots\cdot} + Fe^{\cdot\cdot}.$$

Reduction, the converse of oxidation, is, like the latter, essentially a valency change, and oxygen need not even be present in the system.

* See Knecht and Hibbert, *New Reduction Methods* (Longmans).

THE COLLOIDAL STATE

95. Some knowledge of colloid behaviour is desirable for the successful practice of analytical chemistry.

Since Thomas Graham * first distinguished substances as crystalloids and colloids, according as they were able or unable to diffuse through certain membranes, very great advances have been made in our knowledge of this subject, which is now treated as a special branch of chemistry.†

Graham worked with a great variety of materials, and found that many insoluble substances could be made to assume the colloidal form. Since his day it has been shown that there is no definite relationship between chemical constitution and colloid state. While it is true that many natural products of complex constitution, such as the proteins, cellulose, starch, occur as colloids, some of these, like egg-albumen and haemoglobin, have been crystallised ; and on the other hand quite simple substances like common salt and the metals can assume the colloidal form. Practically all substances can be obtained in the colloidal state, which is, in the words of von Weimarn, " a universally possible state of matter," and the study of colloid chemistry is really the study not of special groups of compounds but of the colloidal condition of matter.

96. Dispersoids. The so-called colloidal solutions are not true solutions of the type of the molecular and ionised solutions. Their physical properties, such as osmotic pressure, which is very low, are not in accordance with this view. They are really suspensions of matter in an extremely fine state of division, and are thus two-phase systems. The size of the particles is about 100 $m\mu$ to 1 $m\mu$, or from one ten-thousandth to one millionth of a millimetre. The existence of these particles is revealed by their optical behaviour, in that they render visible the path of a beam of light in an otherwise dark fluid, a method first used by Faraday

* *Trans. Royal Soc.* **151,** 183 (1861).

† See Wolfgang Ostwald's *Handbook of Colloid Chemistry* (Churchill, 1919).

(1857) for gold sols, and extended by Tyndall in 1869 (Tyndall phenomenon). They also show the Brownian * movement by the agency of the ultramicroscope,† the principle of which is to detect the presence of particles by the light reflected from them in a dark field.

Such liquids therefore pass without change through ordinary filters and even through most of the fine porcelain and clay filters, and are thus differentiated on the one hand from the coarser suspensions, which may be filtered. On the other hand they differ from the molecular dispersions or true solutions in that they do not diffuse and do not dialyse, which molecular solutions do. Further, there exist transition systems not only between coarse dispersions and colloids, but between colloids and molecularly dispersed solutions. The colloids merely represent a realm differentiated for practical purposes from a continuous series of systems.‡

Colloidal liquids may be divided into two classes :

(*a*) Suspensoids, or suspension colloids, in which the disperse phase is a solid, while the continuous phase is a liquid ;

(*b*) Emulsoids, or emulsion colloids, in which, as in an emulsion, both the continuous and the disperse phases are liquids.

97. Preparation of Colloids.§ Arsenious Sulphide. When sulphuretted hydrogen is passed into an aqueous solution of arsenious oxide or sodium arsenite no precipitate is obtained, but the liquid becomes yellow and opalescent. It passes through a filter, and may be preserved unchanged for a long period. It contains arsenious sulphide in the colloidal form. On addition of a little hydrochloric acid, or a salt solution, the sulphide is at once precipitated.

* First observed with pollen grains in water, by Robert Brown, botanist, 1827.

† Zsigmondy, *Colloids and the Ultramicroscope* (1909).

‡ Wo. Ostwald, *Introduction to Colloid Chemistry*, 21 (1917).

§ A. A. Noyes, *J. Amer. Chem. Soc.* **27**, 86 (1905).

Ferric hydroxide, precipitated by the careful addition of ammonia to a solution of ferric chloride, dissolves at first in the excess of ferric chloride, forming a dark reddish-brown solution. When this is placed in a parchment thimble or other form of dialyser, the ferric and ammonium chlorides diffuse into the water outside, leaving ferric hydroxide in the colloidal form. Such colloid preparations are used medicinally under the name of dialysed iron.

Gold, silver and other metals may be obtained in the colloidal form in many ways. Bredig's * method is to make a short electric arc (110 volts) between terminals of the metal under water; intensely coloured liquids are obtained. Many reduction reactions also give colloidal forms of the metals. Thus very dilute solutions of gold chloride may be reduced by warming with very dilute solutions of stannous chloride (purple of Cassius), or of tannic acid or hydrazine hydrochloride. Very sensitive colour reactions for the noble metals are given also by the use of the ordinary borax bead; the bead is moistened at the frothing stage with a very dilute solution of the metallic salt. On fusing, the metal forms a colloidal dispersion in the borax, the colour varying with the nature of the metal and its degree of dispersion. Donau † has shown that these borax colour reactions are in some cases more delicate than spectro-analytic ones.

98. Electrical properties of colloids. In a large class of colloids the suspended particles carry electrical charges, thus creating a difference of potential between the particles and the liquid in which they are suspended.‡ This may be shown by passing a current from a few storage cells, or more quickly with one of 200 volts, between platinum terminals in a U-tube filled with the liquid. The particles migrate towards one or the other electrode according to their electric sign (*cataphoresis*). But they do not obey Faraday's law that one gram-equivalent of an ion is deposited for each 96,500 coulombs. The colloid particles are

* Bredig, *Anorganische Fermente*, 1901.

† J. Donau, *Koll.-Zeitschr.* **2,** 273 (1908).

‡ Picton and Linder, *J. Chem. Soc.* **61,** 160 (1892); **71,** 568 (1897).

more complex than molecules, and the deposit may be 6–8 times as much. Electro-negative colloids include sulphides (As_2S_3, CdS), metals, and acids like silicic and stannic. Ferric and other metallic hydroxides, and basic dyes, are positively charged and migrate towards the cathode.

The source of the charge on colloid particles is believed to be a partial ionisation which leaves charged ions in the suspended particles. This view is supported by the fact that silicic and other acids change the sign of their charge on the change of the medium from acid to alkaline. In alkaline or weak acid liquids, which favour ionisation as an acid, silicic acid carries a negative charge ; in presence of strong acid, however, the charge is positive, as it would be if the particles, like those of ferric hydroxide, retained positive ions. Another factor in causing the electric charge is the general effect that particles suspended in a liquid of different dielectric constant become electrically charged. When, as is usually the case, the dielectric constant of the liquid is higher than that of the suspended particles, the latter become negatively charged. This is true not only of coarse suspensions such as clay, but also of the much finer dispersions known as colloids. Most colloids become negatively charged in water, though positive colloids such as ferric and aluminium hydroxides are also known. A full explanation is not yet available, but there is little doubt that these electric charges on the particles help in maintaining the dispersion of the colloid.

99. Precipitation of colloids. Such electrically charged colloidal suspensions are readily precipitated by the addition of electrolytes, as in the case of arsenic sulphide. The precipitation follows Hardy's rule,* that negatively charged colloids are precipitated by the action of positive ions, and *vice versa*. The precipitating power of electrolytes increases largely with the valency of the precipitating ions † ; for the same quantity of As_2S_3, 51·0 g. of NaCl, or 0·65 g. $CaCl_2$, or 0·09 g. $AlCl_3$ are required.

Colloids are also precipitated by other colloids carrying an

* Hardy, *Proc. Royal Soc.* **66**, 110 (1899).

† H. Schulze, *J. prakt. Chemie* [2], **32**, 390 (1885).

opposite charge. Thus arsenious sulphide and ferric hydroxide mutually precipitate each other, the precipitated gel being an adsorption complex of the two substances. The precipitation takes place in the proportions in which the colloids neutralise each other's charges, and if these proportions are departed from the precipitation is incomplete. If a large excess of either be used, no precipitation at all may occur.

100. Adsorption is a general phenomenon involving a change of concentration of material at the surface of separation of two phases. Positive adsorption is an increase of concentration at a surface, and is a contributory cause of many surface- or wall-reactions. Negative adsorption is a decrease of concentration.

Willard Gibbs showed thermodynamically (1899) that if a solute lowered the surface tension of a solution at its interface, the concentration of the solute in this interfacial layer would be greater than in the rest of the solution.

The material which adsorbs another is called the *adsorbent*, while the substance adsorbed is the *adsorbate*. Porous materials in which there is a large extension of surface are naturally the most efficient adsorbents. The property of charcoal of adsorbing gases has been known since the time of Scheele, and is reversible, being greater at low temperatures. It is non-specific, and not dependent on any chemical reaction with the adsorbate. It does depend, however, on the molecular weight of the latter; gases and vapours of high molecular weight and high boiling point are the most readily and completely adsorbed by activated charcoal. This fact is of great importance. It is the cause of the varying efficiency of gas-masks, containing charcoal, as protection against different poison-gases or vapours. Heavy vapours like mustard-gas, which boils at 217°, are very easily adsorbed.* The use of charcoal in decolorising solutions of sugar and other organic substances is due to adsorption of the colouring matter. Silica gel (177) has been much employed in various reactions also because of this property. Adsorption is also a preliminary stage, followed by chemical changes, in the processes of dyeing and tanning.

* See J. B. S. Haldane, *A.R.P.* (*Appendix II*) (1938).

Adsorption is one of the most characteristic properties of colloids, and arises from their great surface development. Wilhelm Ostwald pointed out that in contact surfaces between solids and liquids, the concentration of a dissolved substance is always greater than in the rest of the solution.* The phenomenon occurs only with colloidal (amorphous) precipitates, and greatly increases the difficulty of washing these. In the precipitation of colloids with electrolytes, the precipitating ion is to some extent carried down with the colloid,† the amount of the ion so adsorbed by a given weight of a given colloid being proportional to the equivalent weights of the ions. Polyvalent ions are adsorbed more readily than univalent, and organic ions to a greater extent than inorganic. The fraction of the total amount of substance adsorbed is greater the more dilute the original solution. Von Weimarn has shown ‡ that the amounts of electrolytes adsorbed by a constant weight of barium sulphate increase with the diminution of the solubility of the electrolyte in the solvent used.

101. Applications in analysis. The colloidal state is clearly one to be avoided as far as possible in analytical operations. In the formation, filtration and washing of precipitates, those conditions that encourage the production of colloid forms should be excluded. One of the most important of these is *absence of electrolytes*, a condition which is approached in the washing of precipitates.§ During this operation precipitates often appear to pass through the filter. The explanation frequently is that the substance forms a colloidal suspension with pure water, which is reprecipitated on mixing with the electrolytes in the filtrate. To avoid this the precipitate may be washed with a solution of some ammonium salt which does not interfere with its subsequent treatment, as ammonium sulphide for the sulphides of the zinc group.

For similar reasons, precipitation should not be made in very

* Wilhelm Ostwald, *Foundations of Anal. Chem.*, p. 19.

† Picton and Linder, *J.C.S.* **67**, 63 (1895).

‡ P. P. von Weimarn, *Chemical Reviews*, **2**, 229 (1925).

§ Julius Stieglitz, *Qualitative Analysis*, **1**, 131 (Bell, 1922).

dilute solutions, or in presence of weak electrolytes only. Addition of salts may then be necessary to induce precipitation, as in the case of arsenic sulphide. High temperature, concentration and the lapse of time (standing overnight) all tend to reduce the degree of dispersion of colloids and complete their precipitation.

Gelatinous precipitates such as the hydroxides of copper and the metals of the iron group are known to be difficult to wash. Sodium hydroxide molecules are adsorbed, as well as the ions of sodium and hydroxyl, and are difficult to remove. The iron group hydroxides similarly tend to adsorb salts and ions of the zinc and barium groups, and if these are present in large amounts the adsorption becomes important in quantitative separations. In such cases a second precipitation is desirable.

The adsorption indicators used in some volumetric precipitation reactions are a notable application of this phenomenon. The colouring of silver halides by certain dyes was noted by Hübl in 1894, and examined by Kieser in 1904, in relation to photographic sensitising; but was first explained and applied in analysis by Kasimir Fajans in 1923.* The colour change may be observed in extremely dilute solution of the indicator, say sodium fluoresceinate or eosinate, to which a few drops of N. silver nitrate solution are added. No change of the yellow-red colour is produced, but on adding one drop of N. potassium bromide solution, the colour deepens, becomes more red, and at the same time the fluorescence diminishes. Silver bromide has been formed, as a colloid sol, with great surface development, and the sol particles have formed a positively charged silver body $[AgBr]Ag^{\cdot}$ which adsorbs the anion of the colour. In the ordinary titration this adsorption occurs on the surface of the precipitated silver halide, which becomes pink as soon as free silver ions are present. Many applications of this method have been made (**465**).

* Fajans and Hassel, *Z. Electrochem.*, **29**, 495 (1923). I. M. Kolthoff, *Chem. Reviews*, **16**, 87 (1935). Fajans, *Newer methods of analysis* (ed. W. Böttger), 203 (1938).

PREPARATIONS

INSTRUCTIONS TO STUDENTS

BEFORE commencing a preparation make certain that you understand the reactions involved. Read carefully through the whole of the instructions, and if anything is not clear, have it explained before proceeding. The quantities of materials to be used are in most cases given. Compare them with the formula weights, and if the proportions do not agree, that is, if an excess of one or other material is employed, find out why this is so.

In cases where an apparatus has to be devised, or put together from a description in the text, make a drawing of the apparatus you propose to use, and submit it for approval. When the apparatus has been fitted up, do not commence the experiment until it has been examined and approved by the teacher. In all cases follow carefully the instructions given.

Enter all work in the note-book at the time of observation, leaving nothing to be written up afterwards from memory. If your observations do not agree with the text, make a note of the fact. Weigh all finished products, and note the amount in your book. Calculate wherever possible the theoretical yield of product from the quantity of the original substance used, and deduce the percentage of the theoretical yield obtained in your experiment. Make a note, so far as you can, of reasons for the deficiency.

Before throwing away any liquors or residues, consider carefully whether you can make any further use of them.

PREPARATION OF THE GASES REQUIRED IN SUBSEQUENT EXPERIMENTS

For the experiments involving the use of a gas, a constant stream will be required. The following methods will be found

convenient. If the gas be required dry, reference should be made to par. 22.

102. Chlorine. The liquid chlorine now supplied in cylinders is made by the electrolysis of brine (154). The gas passes through stoneware H_2SO_4 drying towers, then by means of cast-iron pumps at three atmospheres pressure to liquefying coils at $-35°$ C.

The gas can be obtained from common salt as follows :

In a flask of $1\frac{1}{2}$ litres capacity fitted with a good cork, safety funnel and delivery tube, place a cold mixture of 110 c.c. water and 150 c.c. conc. sulphuric acid. To this add an intimate mixture of 120 g. common salt with an equal weight of powdered manganese dioxide. There is no action in the cold, but on warming the mixture on a sand-bath or in a water-bath a slow and continuous stream of chlorine is evolved. The gas should be washed with water to free it from hydrochloric acid, and dried if necessary.

The above quantities will give about 20 litres of chlorine. In cases where exact amounts of chlorine are required, the method given for hypochlorites (116) is a good one.

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

Chlorine may also be obtained in the laboratory by heating hydrochloric acid with potassium dichromate or manganese dioxide, the substance used by Scheele when he discovered the gas in 1774.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$

Chlorine is used for making hydrogen chloride, bleaching powder and other hypochlorites, chlorates and perchlorates, and many chlorides, both inorganic and organic.

103. Hydrogen. A Kipp's generator is charged with commercial granulated zinc and a mixture of equal volumes of conc. hydrochloric acid and water, or a cold mixture of one volume of conc. sulphuric acid with two volumes of water.

The gas liberated by ordinary zinc contains small quantities of

arsenic and antimony hydrides. These may be removed by washing the gas through potassium permanganate.

Hydrogen is manufactured in the electrolysis of brine, and by passing steam over white-hot coke to obtain water-gas ($H_2 + CO$). It is used for the manufacture of ammonia (Haber process), methanol (190), hydrogen chloride, and in the catalytic hydrogenation of unsaturated fats, oils and gases.

104. Hydrogen chloride. A Kipp's generator with lumps of rock salt or fused common salt and concentrated sulphuric acid is convenient, and supplies the gas practically pure and dry.

The method used for chlorine (102), without the manganese dioxide, is also convenient ; no gas is liberated until the mixture is warmed. The spent acid may be used for making Glauber's salt (113).

The gas is now manufactured from electrolytic hydrogen and chlorine, burning the latter in excess of hydrogen in silica ware burners. The product, absorbed in distilled water, gives a very pure acid containing 35–38 per cent. HCl.

105. Ammonia. The gas can be obtained pure by heating a mixture of pure ammonium chloride and lime. For most purposes it may be obtained sufficiently pure by warming the conc. aqueous solution, and drying the evolved gas in a lime tower (Fig. 28). If much gas is to be prepared a preliminary partial drying can be effected by passing the gas through a small quantity of its own saturated solution contained in a wash bottle cooled by ice and salt.

106. Carbon dioxide. Chips of marble, and hydrochloric acid diluted with an equal volume of water, form the most convenient source of the gas. A Kipp's apparatus is usually kept charged and ready for use. The gas should be washed in water to free from hydrochloric acid.

Small quantities of the gas may also be made by heating sodium bicarbonate or magnesium carbonate.

107. Carbon monoxide. When formic acid or oxalic acid is heated with conc. suiphuric acid, carbon monoxide is evolved,

in the latter case mixed with an equal volume of carbon dioxide.

$$H \cdot COOH = H_2O + CO.$$

$$(COOH)_2 = H_2O + CO + CO_2.$$

1. In a small distilling flask heat some concentrated sulphuric acid, and allow formic acid to drop slowly in from a tap funnel. Collect the gas over water.

2. From oxalic acid the gas may be obtained by heating 50 g. crystallised oxalic acid with enough conc. sulphuric acid to cover it. The carbon dioxide is removed by passing the evolved gases through a strong solution of caustic potash.

3. Potassium ferrocyanide also gives carbon monoxide when heated with conc. sulphuric acid.

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO.$$

Cover the powdered ferrocyanide in a small flask with conc. sulphuric acid and heat over wire gauze. The action is easily regulated, and the supply of gas may be stopped by cooling the flask. The gas should be washed in a conc. solution of caustic soda or potash. Carbon monoxide is absorbed by either an ammoniacal or a hydrochloric acid solution of cuprous chloride.

108. Sulphur dioxide. The liquid sulphur dioxide supplied in syphons is very pure. If this is not available the gas can conveniently be prepared by dropping conc. sulphuric acid from a tap-funnel on to a quantity of solid sodium bisulphite or of the commercial bisulphite solution, contained in a bottle or flask. Sulphur dioxide is immediately liberated. The gas is a reducing agent and can be removed from mixtures with many other gases by passage through a solution of potassium dichromate.

109. Sulphuretted hydrogen. Ferrous sulphide is readily decomposed by dilute hydrochloric or sulphuric acid, liberating sulphuretted hydrogen. The gas may be generated in a Kipp's apparatus. Hydrochloric acid (equal volumes of acid and water) is preferable to sulphuric acid, as ferrous chloride is more soluble

than the sulphate, and there is therefore less risk of the salt crystallising and blocking the apparatus. The gas should be washed with water to remove hydrochloric acid.

Since sulphide of iron often contains particles of free iron, the gas obtained in this way contains a little hydrogen. For ordinary purposes, however, this is not objectionable.

Many forms of apparatus are employed for the preparation of sulphuretted hydrogen. Any apparatus used for hydrogen or carbonic acid gas, such as a Woulff's bottle with thistle funnel and delivery tube, will also serve for the preparation of sulphuretted hydrogen. When a large quantity of the gas is required, this may be made by using two large bottles connected with each other by means of rubber tubing passing between tubulures at the bottom, one bottle containing sulphide and the other the acid. The acid bottle is raised or lowered when necessary.

In most forms of generator the acid is largely wasted, partly because of the imperfect arrangement for mixing the acid, as in the Kipp's generator, and also because the acid when nearly neutralised ceases to act sufficiently rapidly on the sulphide. It therefore has to be renewed before it is exhausted. To obviate this, the method may be used of dropping the acid slowly on to the sulphide contained in a tall glass tower. Before the liquid reaches the bottom of the column of sulphide the acid is in general almost completely neutralised. If required dry, concentrated sulphuric acid should not be used owing to the reducing action of the gas :

$$3H_2S + H_2SO_4 = 4H_2O + 4S.$$

Phosphorus pentoxide or calcium chloride may be used.

INORGANIC COMPOUNDS

THE ALUMS

110. The alums have the general formula

$$R_2SO_4 . M_2(SO_4)_3 . 24H_2O,$$

where R is a univalent cation and M is either aluminium or iron, chromium, manganese, etc. The alums are all isomorphous.

Crystallisation of potash alum, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$. Dissolve about 200 g. of potash alum in 1,400 c.c. of hot water, filter if necessary and allow to cool. If crystals separate on cooling, add water to dissolve them. Allow the solution to stand in a large crystallising dish (Fig. 9), covering the dish with a sheet of paper to protect the solution from dust. From the crystals first formed pick out those free from adhering crystals. Transfer the clear solution to a similar dish, place the selected crystals in it and allow them to grow. Each day, if necessary, remove the selected crystals and place them in the clear solution as before, after redissolving any smaller crystals which may have separated. The crystals will be octahedral in shape, but unless turned (par. 13) on different faces, to allow each face the same opportunity to grow, irregular octahedra will be obtained.

The 200 g. of alum may be replaced by molecular proportions of potassium sulphate, K_2SO_4, and aluminium sulphate, $Al_2(SO_4)_3 . 18H_2O$.

9·5 g. of potash alum dissolve in 100 g. of water at 10°.

Alum is chiefly used as an aluminium mordant in dyeing, in the manufacture of lakes, and as an astringent.

Crystallisation of chrome alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$. The solution obtained in the preparation of aldehyde may be used (200), or one prepared by passing sulphur dioxide into a solution of 50 g. of potassium dichromate and 20 g. of sulphuric acid in one litre of water, until the reduction is complete. The temperature should not exceed 60–70° during the reduction and subsequent crystallisation. Otherwise the alum is obtained in the green modification, which is more soluble and more difficult to crystallise. The crystals are obtained as in the previous preparation. They are isomorphous with those of potash alum (compare them), and crystals of either substance, when placed in a saturated solution of the other, will continue to grow (par. 12).

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

The crystals of chrome alum are deep violet in colour and are efflorescent. They melt in their water of crystallisation at 89°.

Chrome alum is used as a chrome mordant, and in chrome tanning.

111. Ferrous ammonium sulphate, $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$. Dilute 50 c.c. of concentrated sulphuric acid to 200 c.c., pouring the acid into the water in small quantities at a time, and mixing after each addition. Neutralise one-half with ammonium hydroxide, boiling to expel any excess of ammonia, and warm the other with iron filings (in the fume cupboard) till no more iron will dissolve. Filter the solutions into the same crystallising dish, add a few c.c. of dilute sulphuric acid to prevent the formation of basic sulphate of iron by hydrolysis (88), and allow to crystallise.

$$H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + 2H_2O.$$

$$H_2SO_4 + Fe = FeSO_4 + H_2.$$

The substance may be purified by recrystallisation.

Molecular proportions of ferrous sulphate, $FeSO_4 . 7H_2O$, and ammonium sulphate, $(NH_4)_2SO_4$, may be used.

Ferrous ammonium sulphate crystallises in transparent bluish-green monoclinic crystals, and being stable in the air, is used for the standardisation of solutions in the volumetric estimation of iron. 17·5 g. of the salt dissolve in 100 g. of water at 12°.

112. Nickel potassium sulphate, $NiSO_4 . K_2SO_4 . 6H_2O$, **and copper ammonium sulphate,** $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$, may be prepared from molecular proportions of the sulphates. The crystals should be compared with each other and with those of ferrous ammonium sulphate.

113. Sodium sulphate (Glauber's salt), $Na_2SO_4 . 10H_2O$. In the preparation of hydrogen chloride (104), the temperature is not high enough to yield sodium sulphate, the salt-cake of the old Leblanc soda process; the residue is mainly sodium bisulphate. Dissolve this in water, neutralise with sodium hydroxide solution, filter and evaporate to crystallising point. The decahydrate separates from cold solutions in efflorescent monoclinic prisms.

There is also an unstable heptahydrate. Sodium sulphate readily gives supersaturated solutions. The solubility curve (Fig. 8) shows a maximum solubility at 32° (decahydrate); above this point the solubility is that of the anhydrous salt and diminishes with increase of temperature.

Sodium sulphate is exported in large quantities to Scandinavia, for use in the manufacture of wood pulp. It is applied also in the manufacture of glass, in the dyeing of wool and cotton, and as Glauber's salt in medicine.

114. Potassium nitrate, KNO_3. Weigh out molecular proportions of potassium chloride, KCl, and sodium nitrate, $NaNO_3$, dissolve the mixture in boiling water, evaporate till crystals of sodium chloride begin to settle out, filter hot and allow to cool. Crystals of potassium nitrate form and may be purified by recrystallisation. The mother liquor should be evaporated for a second crop of potassium nitrate crystals.

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

As Chile saltpetre contains chlorides, bromides, iodides and sulphates of sodium and magnesium with traces of iron salts, it should first be purified or a pure sodium nitrate used.

The solution will contain the chlorides and nitrates of sodium and potassium in equilibrium with their ions. On evaporation, the substance with the smallest solubility product will crystallise first. At ordinary temperatures this is potassium nitrate, but, at boiling point, sodium chloride will be precipitated. See also the solubility table (Appendix).

Potassium nitrate crystallises in long rhombic prisms. It is largely used in pyrotechnics, in making gunpowder and other explosives, and in the laboratory as an oxidising agent.

115. Purification of common salt. Make 500 c.c. of a saturated solution of common salt in water. Place the clear solution in a wide beaker and pass in hydrochloric acid gas. Owing to the great solubility of the gas in water, the liquid must be prevented from rushing back into the generator.

This can be effected by delivering the gas from the mouth of an inverted funnel dipping just below the surface of the liquid. One impurity in common salt is magnesium chloride, which, by its deliquescence, causes the salt to become damp when exposed to the air.

The hydrochloric acid increases the [Cl′] and the solubility product of the sodium chloride is soon reached. Pure sodium chloride is therefore precipitated. Owing to the small [Mg˙˙] and the great solubility of magnesium chloride, the solubility product of magnesium chloride is not reached, and this, with other impurities, remains in solution.

Filter by suction, wash with pure concentrated hydrochloric acid, partially dry with filter paper, then in the air oven, and finally by heating in a porcelain dish, to remove the last traces of hydrochloric acid.

PREPARATION OF VARIOUS COMPOUNDS BY THE DIRECT ACTION OF CHLORINE

116. Sodium hypochlorite,* NaOCl. When chlorine gas is passed into a cold solution of caustic potash or soda, a mixture of chloride and hypochlorite is obtained.

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

The reaction is quantitative, and can be employed to prepare solutions containing definite amounts of the hypochlorite.

The chlorine may be prepared by the action of potassium permanganate on hydrochloric acid.

Weigh out 25 g. of potassium permanganate and place in a half-litre distilling flask fitted with a tap funnel. Arrange to pass the chlorine first through a wash bottle containing water to remove hydrochloric acid and then into a solution of 50 g. caustic soda in 400 c.c. water, contained in a bottle surrounded by ice so that the temperature may be kept below 5°. To the permanganate add slowly 150–170 c.c. conc. hydrochloric acid by means of the tap funnel. The reaction is at first instantaneous,

* Graebe, *Berichte*, 35, 2753 (1902).

chlorine being evolved, but towards the end the liquid should be heated until all the permanganate is reduced and no more chlorine is obtained.

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

The chlorine is completely absorbed by the soda. Now make the solution of hypochlorite up to 500 c.c. ; calculate the quantity of hypochlorite contained therein and estimate the amount by the method given in **456**. If the experiment has been well conducted, almost the theoretical amount will be found.

117. Potassium chlorate, $KClO_3$. Chlorine gas acts differently from the above on hot solutions of caustic alkalis, producing a mixture of chlorate and chloride.

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Dissolve 50 g. caustic potash in 250 c.c. water in a half-litre beaker, and heat on a sand-bath to 65°–75° throughout the experiment. Pass in chlorine gas prepared by one of the methods given, using a little more than the quantities of material which will supply the necessary chlorine. The gas should be washed in water to remove hydrochloric acid, and is introduced into the alkali by means of an inverted funnel just touching the surface of the solution. When the reaction is over, filter the solution if necessary and evaporate slowly to about 180–170 c.c. On cooling, potassium chlorate will crystallise but the chloride will remain in solution. Filter at the pump, wash the crystals twice with small quantities of cold water and set aside to dry. Concentrate the filtrate further and examine each crop of crystals for chlorate and chloride. Yield of chlorate, 10–15 g.

Chlorates of potassium and sodium are now manufactured by electrolysis of solutions of the chlorides above 45° C., the electrodes being close together and the liquid under constant agitation. Potassium chlorate crystallises in monoclinic tables, melting at 334° and decomposing at 352°. It is less soluble than the sodium salt.

118. Potassium chloride, KCl, may be obtained by recrystallising the later crops in the last experiment. It is isomorphous with

sodium chloride, but more soluble. Large quantities are now obtained from the Dead Sea (Palestine Potash Ltd.) by recrystallising the carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, which separates on evaporation. Bromine is obtained from the mother-liquors.

119. **Potassium perchlorate**, $KClO_4$. This can be prepared by carefully heating the chlorate until a small sample of the melt, warmed with hydrochloric acid, gives little or no chlorine :

$$4KClO_3 = 3KClO_4 + KCl.$$
$$2KClO_3 = KClO_4 + KCl + O_2.$$

It is now manufactured, like the ammonium salt, by double decomposition of sodium perchlorate with potassium or ammonium chloride :

$$NaClO_4 + KCl = KClO_4 + NaCl.$$

Sodium perchlorate, $NaClO_4 \cdot H_2O$, is made by the low temperature electrolysis of strong solutions of the readily soluble chlorate. The potassium salt is anhydrous, sparingly soluble in water and less so in alcohol. It may be used for the estimation of potassium (521 C). The ammonium salt is used as an explosive ; it leaves no solid residue. Magnesium and barium perchlorates are good drying agents (22).

120. **Anhydrous ferric chloride**, $FeCl_3$. A piece of combustion tube about 10 inches long is fitted at each end with a cork carrying a tube so that dry chlorine gas may be passed through, the excess being absorbed in caustic soda. A porcelain boat is filled with iron filings free from grease (by washing with benzene if necessary) and inserted in the combustion tube near to the end at which the chlorine enters. The iron is heated to dull redness in the stream of dry gas, and anhydrous ferric chloride sublimes on to the cool part of the tube and is there deposited in dark brown hexagonal plates which have a metallic lustre and appear red by transmitted light. The crystals are deliquescent and easily soluble in water, alcohol and ether. They should be transferred to a tube and sealed up.

121. **Aluminium Chloride**,* $AlCl_3$. Arrange an apparatus similar to that used for ferric chloride, but use a longer combustion tube,

* Gattermann, *Practical Methods of Organic Chemistry* (Macmillan and Co. Ltd.).

and heat in a small furnace (Fig. 52). The tube is charged with clippings of aluminium foil, and the chloride, which is very hygroscopic, should be sublimed directly into a dry bottle into which the

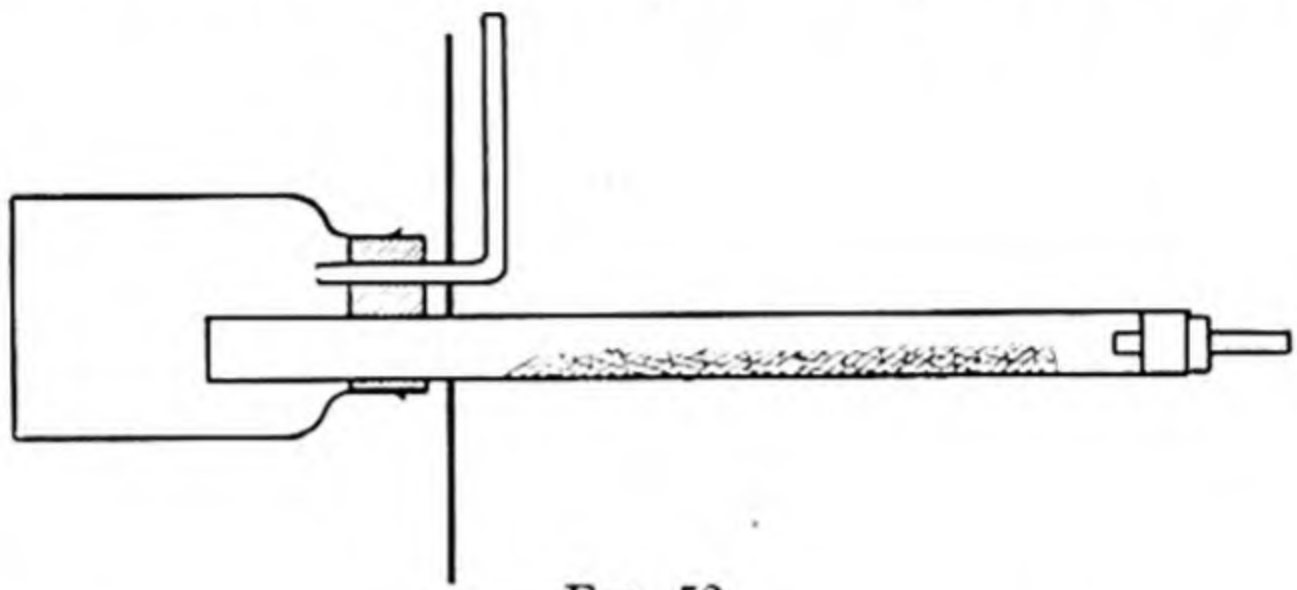


FIG. 52.

end of the combustion tube is inserted through a gas-tight cork, and from which the excess of chlorine is conducted to an absorber. It is manufactured by heating a dried mixture of bauxite, as free as possible from iron and silica, with coke or a coking coal, to 800°–850° C. in chlorine.

Pure aluminium chloride forms colourless hexagonal crystals. The yellow colour of the commercial product is due to traces of ferric chloride. It is used in organic synthesis (291), and is soluble in alcohol, ether, pyridine and other organic liquids. The hydrate, $AlCl_3 . 6H_2O$, separates on saturating the aqueous solution with HCl.

122. Chromic chloride, $CrCl_3$. Use the same apparatus as for aluminium chloride, but without the bottle as receiver. Grind up 5 to 10 grams of chromium sesquioxide and an equal weight of starch into a thick paste with a little cold water. Mould this into balls of the size of peas, dry these carefully and heat on an iron tray until the starch is completely charred. Transfer to the combustion tube and heat to redness in the stream of dry chlorine. Chromic chloride is obtained in beautiful violet scales, almost insoluble in cold water.

123. Stannic chloride, $SnCl_4$. In a wide glass tube about a foot long and closed at one end, fit an upright condenser and a delivery tube. Fill the wide tube with granulated tin and pass in dry

chlorine gas. The delivery tube should reach at first to the bottom, and should be withdrawn as the liquid tin chloride forms, so that the end just dips into the liquid. When nearly all the tin is converted into chloride, pour the liquid into a dry distilling flask and collect the portion boiling at 118–122°.

Tin tetrachloride is a colourless, mobile liquid, fuming in air; sp. gr. 2·234 at 15°; b.p. 120°. It forms several hydrates with water, of which the crystalline pentahydrate, $SnCl_4 . 5H_2O$, is used as a mordant in dyeing.

124. Phosphorus trichloride, PCl_3. Place 10 g. phosphorus in a small retort. Insert the stem through a good cork into a distilling flask as receiver, and on the side tube of this, place a small calcium chloride tube. From this lead a tube to an absorber for the excess of chlorine.

Pass dry chlorine gas over the phosphorus and heat the retort gently on a sand-bath. If any solid pentachloride is formed, raise the delivery tube further from the phosphorus. The receiver should be kept cool in a vessel of water. Redistil the trichloride, keeping out moisture in a similar manner.

Phosphorus trichloride forms a colourless, fuming liquid; sp. gr. 1·613 at 0°; b.p. 76°. The vapour is very irritating and poisonous.

125. Phosphorus pentachloride,* PCl_5. Fit up an apparatus like that shown in Fig. 53. Through the upper delivery tube dry chlorine is admitted, the excess leaving by the lower tube which is protected from moisture by a calcium chloride tube. Phosphorus trichloride is introduced, a few c.c. at a time, from the tap funnel, and when the pentachloride formed appears quite dry, the reaction is over. Thus any desired quantity may be prepared; the chlorine delivery tube is raised to keep clear of the pentachloride, and if necessary it may be cleared by means

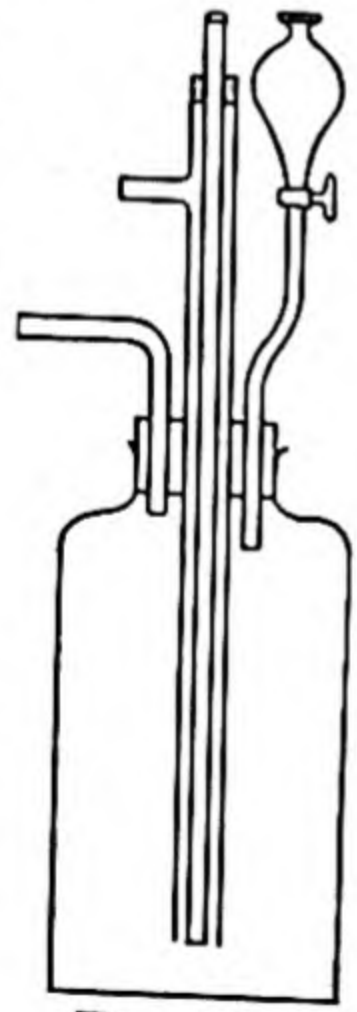


FIG. 53.

* Gattermann, *Practical Methods of Organic Chemistry*.

of the glass rod provided. Preserve in the same bottle, well stoppered. Yield, quantitative.

126. Sulphur monochloride, S_2Cl_2. The apparatus used for preparing phosphorus trichloride can also be used for this substance. In the retort place 20 g. dry sulphur, lead in dry chlorine and heat the sulphur gently. It melts and the monochloride distils as a light brown oily liquid. The receiver must be well cooled. The chloride may be purified by redistilling, excluding moisture.

Sulphur monochloride forms a clear, amber-coloured liquid, of sp. gr. 1·7 and b.p. 138°.

127. Sulphuryl chloride, SO_2Cl_2. In a two-necked bottle place 20 g. of camphor, stand the bottle in cold water and lead in dry sulphur dioxide gas so long as it is absorbed. The camphor liquefies. Now pass in dry chlorine until it is no longer absorbed, then sulphur dioxide, and so on until the volume of liquid no longer increases. Transfer to a dry distilling flask and collect the fraction below 100°. Purify by redistillation. The higher boiling portion can be used again to prepare more.

Sulphuryl chloride is a colourless liquid, boiling at 70°. It fumes strongly in air and is decomposed by water into sulphuric and hydrochloric acids.

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

PREPARATION OF CHLORIDES BY MEANS OF HYDROCHLORIC ACID

128. Chlorides of the metals can be prepared by one or more of the following methods.

(*a*) Direct union of chlorine with the metal (120-123).

(*b*) Action of hydrochloric acid on the metal (128-130).

(*c*) Action of hydrochloric acid on the oxide, hydroxide or carbonate of the metal (130, 131, 133, 134).

(*d*) By precipitation of insoluble chlorides, as AgCl.

Examples of the first method have already been given. One or more of the other methods are applicable to the salts of any metal and may be used with other acids than hydrochloric.

129. Anhydrous ferrous chloride, $FeCl_2$. In a bulb tube of combustion glass or a piece of combustion tubing 10–12″ long place a few grams of clean iron filings. Pass dry hydrogen chloride through the tube, and when air is expelled heat the iron filings. The vapour of ferrous chloride condenses on the cooler parts of the tube in colourless, six-sided, shining scales, and by suitable heating may be obtained free from the iron and scraped from the tube. The product should be immediately placed in a dry test-tube which should then be sealed by softening and drawing out.

$$Fe + 2HCl = FeCl_2 + H_2.$$

130. Stannous chloride (tin salt), $SnCl_2 . 2H_2O$. Dissolve 25 g. of granulated tin in 70 c.c. conc. hydrochloric acid, diluted with 25 c.c. of water, in a ½-litre flask, allow the solution to settle and decant from any residue into an Erlenmeyer flask. Close this with a cork and set aside to crystallise. The hydrated salt crystallises in transparent monoclinic prisms which melt in their water of crystallisation at 40° and lose all the water in a vacuum over sulphuric acid. Yield, 35–40 g.

Stannous chloride is a powerful reducing agent, combining with either chlorine or oxygen. When the solution is exposed to air, or diluted with much water, a basic chloride of the composition $2Sn(OH)Cl . H_2O$ is deposited.

131. Zinc chloride, $ZnCl_2$. This may be obtained by neutralising hydrochloric acid with zinc, or its oxide or carbonate. The solution so obtained is evaporated until the temperature reaches 240°. Care must be taken that none of the substance comes in contact with the hands. Allow to cool, break into lumps and bottle immediately, making the stopper air-tight with paraffin.

Zinc chloride forms a white, deliquescent mass. It is used in the laboratory as a dehydrating agent, in surgery as a caustic, and in the textile trade as an ingredient of size. It is also

used as an antiseptic, as a preservative for timber, and in wool dyeing.

132. Cupric chloride, $CuCl_2 . 2H_2O$. Use pure copper oxide, prepared by dissolving copper in nitric acid, crystallising and heating the nitrate until decomposition to oxide is complete. Warm the oxide with dilute hydrochloric acid, using the oxide in slight excess. Filter and allow to crystallise. Rhombic prisms or needles of the above composition separate on standing. These are deliquescent, and are soluble in alcohol.

133. Cuprous chloride, CuCl. (*a*) A small quantity may be prepared as follows : In a test-tube place a few copper turnings, cover with conc. hydrochloric acid, add one or two drops of conc. nitric acid and boil for five minutes. Pour the liquid into water. The cuprous chloride is precipitated as a white powder.

(*b*) Cupric oxide may be substituted for nitric acid.

Place in a $\frac{1}{4}$-litre flask 20 g. of copper, 26 g. of cupric oxide, and 90 c.c. of conc. hydrochloric acid. Connect with an upright condenser and boil for two hours. Pour all the contents into water, filter quickly using suction, and wash the precipitate with sulphurous acid followed by glacial acetic acid. Heat the product in a porcelain dish on the water-bath till no smell of acetic acid can be detected. Keep in a stoppered bottle.

$$Cu + CuO + 2HCl = 2CuCl + H_2O.$$

(*c*) Heat a nearly saturated solution of 50 g. of copper sulphate and 24 g. of common salt to 60–70°. Pass sulphur dioxide through the solution till no further precipitate of cuprous chloride is obtained. Filter, wash and dry as before.

$$2CuSO_4 + 6NaCl + 2H_2O + SO_2 = 2CuCl + 3Na_2SO_4 + 4HCl.$$

Cuprous chloride is insoluble in water, but soluble in hydrochloric acid and in ammonia. These solutions are used for the absorption of carbon monoxide. Acetylene also is absorbed by the ammoniacal solution (562).

134. Calcium chloride, $CaCl_2$. Use the solution of calcium chloride from the carbon dioxide generator. Neutralise the

liquid by boiling with a small amount of milk of lime. This will precipitate any iron present. Allow to settle, pour off the clear liquid as far as possible, and filter the remainder. Evaporate until a portion taken on a glass rod rapidly solidifies. To make the product porous, add a few c.c. of conc. hydrochloric acid before evaporating. Dry by heating in an iron pan, but do not allow the substance to fuse.

Calcium chloride is extremely hygroscopic and is largely used as a desiccating agent. It combines with ammonia, forming the compound $CaCl_2 . 8NH_3$, and cannot therefore be used for drying that gas, or its substitution products.

Crystallised calcium chloride, $CaCl_2 . 6H_2O$, may be obtained by *slowly* evaporating a conc. solution obtained as above.

135. Barium chloride, $BaCl_2 . 2H_2O$. (*a*) **From the carbonate.** Place 100 g. of barium carbonate or powdered witherite in a large porcelain dish and mix to a paste with 100 c.c. water. Add slowly, with constant stirring, a mixture of 75 c.c. conc. hydrochloric acid and 100 c.c. water. Heat finally on the steam-bath and stir well till all effervescence ceases. Now add a slight excess of finely powdered witherite and evaporate to dryness. This precipitates iron, calcium, etc., which commonly occur as impurities in the witherite. Extract the residue with half a litre of boiling water, filter, acidify the filtrate with hydrochloric acid, evaporate to half its bulk and allow to crystallise. Concentrate the mother liquor until no more crystals can be obtained and then recrystallise the whole from distilled water. Yield, about 100 g.

$$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2.$$

(*b*) **From the sulphate.** (i) Mix 50 g. finely powdered barytes (or precipitated barium sulphate) with 10 g. powdered charcoal and heat to bright redness in a covered clay crucible in the muffle furnace for 1–2 hours. When cold, extract the mass with boiling water, filter and add hydrochloric acid to the filtrate till the barium sulphide is all decomposed. Crystallise and purify the barium chloride as above. Yield, about 35 g.

$$BaSO_4 + 4C = BaS + 4CO.$$
$$BaS + 2HCl = BaCl_2 + H_2S.$$

(ii) Mix 20 g. of finely powdered barium sulphate with 80 g. of anhydrous sodium carbonate. Fill a fireclay crucible with the mixture and heat in the muffle furnace till fused. Add more of the mixture and again heat. Repeat until the whole is fused in the crucible and heat strongly for half an hour. Allow to cool, lay the crucible on its side in water in a porcelain dish and boil to extract the soluble matter. (It will be found better to break the crucible and powder the contents before boiling with water.) Wash the residue by decantation through a filter paper. Add dilute hydrochloric acid to the residue in the dish until there is no further effervescence. Boil and filter through the same filter paper. The yellow colour of the filtrate is due to traces of iron from the crucible ; this can be removed as in method (*a*). Evaporate the filtrate and allow to crystallise. The yield is not good.

Barium chloride is manufactured from barytes by roasting the powdered mineral with powdered coke, limestone and calcium chloride. The product is lixiviated and the barium chloride crystallised. The student may try this method.

136. Chromyl chloride, CrO_2Cl_2. Mix 10 g. of powdered potassium dichromate with 8 g. of sodium chloride, and place the mixture in a retort. Cover with concentrated sulphuric acid and distil :

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = K_2SO_4 + 2Na_2SO_4 + 3H_2O + 2CrO_2Cl_2.$$

Red fumes are evolved, which condense in the neck of the retort to a dark reddish brown liquid, boiling at 116°. The distillate may be collected in a dry flask placed over the end of the retort and resting in cold water.

Chromyl chloride may also be prepared by making a solution of chromium trioxide in concentrated sulphuric acid, adding hydrochloric acid, drop by drop, and then distilling.

Chromyl chloride is decomposed by water, giving a solution of chromic acid and hydrochloric acid. Its formation is used to detect chlorides in presence of bromides (see par. 331, 3).

BROMINE AND IODINE COMPOUNDS

137. Hydrobromic acid, HBr. The method used for hydrochloric acid (104) is unsuitable for hydrobromic and hydriodic acids. In a flask fitted with tap funnel and delivery tube place 5 g. red phosphorus and 15–20 c.c. water. Allow 10 c.c. (30 g.) of bromine to drop slowly from the funnel. Hydrobromic acid is produced.

$$5Br + P + 4H_2O = H_3PO_4 + 5HBr.$$

To free the gas from bromine, conduct it through a U-tube containing moist asbestos dusted with red phosphorus, and absorb the gas in 100 c.c. of water by means of an inverted funnel or retort, or a large pipette, just dipping into the liquid. Distil the acid and collect the constant boiling liquid (123–129°).

138. Potassium bromide, KBr. (*a*) Place 20 g. fine iron filings and 200 c.c. water in a flask, and add slowly 30 g. (10 c.c.) bromine, shaking well after each addition. Bromides of iron are produced. To the liquid add now a solution of 25 g. potassium carbonate as long as a precipitate is formed. Heat nearly to boiling, filter from the excess of iron and precipitated carbonate of iron, and evaporate the liquid. Potassium bromide crystallises in cubes with a saline taste. It is easily soluble in water and is used in medicine as a sedative. Yield, about 35 g.

(*b*) By the action of bromine on caustic potash, mixtures of bromide, hypobromite and bromate are obtained, according to temperature and concentration of the liquid (compare chlorine). If the liquid be evaporated to dryness and the residue gently ignited, pure potassium bromide is obtained. This should be redissolved and crystallised.

(*c*) Potassium or sodium bromide may also be obtained by neutralising waste hydrobromic acid solution (obtained in brominating benzene, etc.) with potassium or sodium carbonate, after removing free bromine with a stream of air. The dry residue left on evaporation may be used for the preparation of ethyl bromide, etc.

139. Potassium bromate, $KBrO_3$. To a solution of 40 g. caustic potash in 200 c.c. of water, kept at a temperature of 70–80° in a water-bath, add carefully drop by drop 15 c.c. (45 g.) of bromine. Transfer the liquid to a crystallising dish and set aside to cool. Potassium bromate separates, the bromide remaining in solution.

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

It should be recrystallised from hot water and separates in hexagonal crystals, sparingly soluble in cold water.

140. Potassium iodide, KI. This salt can be prepared by the methods given for potassium bromide, but it is best prepared by the action of iodine on caustic potash and ignition of the dry residue. It is very soluble in water, and crystallises in cubes. The solution has a sharp saline taste.

141. Hydriodic acid, HI. This acid may be obtained from iodine, red phosphorus and water, as for hydrobromic acid. Place 5 g. red phosphorus and 20 g. iodine in the flask and add water slowly from the dropping funnel until the mixture is covered. Heat finally on the sand-bath to complete the reaction.

Hydriodic acid is an endothermic compound, and readily acts as a reducing agent. It is so used in many organic reactions.

142. Iodic acid, HIO_3. Place 10 g. iodine in a 250 c.c. round flask fitted with a short condenser, add 100 c.c. *fuming* nitric acid and warm gently until all the iodine is oxidised. Add more nitric acid if required. Nitrogen oxides are evolved.

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

Evaporate to dryness and heat the residue to 200° to remove all trace of nitric acid. Iodine pentoxide remains as a white powder. Redissolve this in a small quantity of water and allow to evaporate, when iodic acid will separate in colourless rhombic crystals. It is easily soluble in water, and is reduced by sulphur dioxide, sulphuretted hydrogen, hydriodic acid, etc., with separation of iodine. When heated to redness, iodine pentoxide is left.

PREPARATION OF METALLIC OXIDES

143. Oxides of the metals can be prepared by one or more of the following methods.

(*a*) Direct union of the metal with oxygen (**144**). Unless the metal is pure, the oxide will be impure. In the production of copper oxide from wire, electrolytic copper can be used.

(*b*) Action of heat on the hydroxide (**145**). A salt of the metal can be purified by crystallisation. To a solution of this pure salt, a soluble hydroxide, preferably ammonium hydroxide, in just sufficient quantity, is added and the precipitate filtered, washed and heated. In the case of copper hydroxide it is only necessary to boil the liquid containing the precipitate to convert the blue hydroxide to the brown hydrated oxide, $2CuO \cdot H_2O$. In some cases the hydroxide is unstable in the cold and the oxide is precipitated instead (**147**).

(*c*) Action of heat on the carbonate. The manufacture of quicklime is an example of this (**74**).

(*d*) Action of heat on the nitrate. As all nitrates are soluble in water, the purified salt can be obtained (**146, 147**).

Special methods are required when the particular oxide is liable to further oxidation if heated in air, or where a readily decomposable peroxide is to be produced (**149**).

144. Cupric oxide from wire, CuO. Pack a length of combustion tubing with copper wire cut into lengths of about one-eighth of an inch, heat the tube to redness in a combustion furnace and pass slowly a current of oxygen (or air) through the tube. In time, the oxidation will be complete and no core of copper will be found when a piece of the product is broken. Cupric oxide thus produced is used in organic analysis.

When heated at the melting point of copper, cupric oxide changes slowly to cuprous oxide :

$$4CuO \rightleftharpoons 2Cu_2O + O_2.$$

Cupric oxide is also produced on heating the nitrate or carbonate, or by boiling the liquid in which cupric hydroxide is precipitated.

The blue hydroxide, $Cu(OH)_2$, loses water, forming brown $2CuO \cdot H_2O$, which yields the anhydrous oxide on heating.

145. Chromium sesquioxide, Cr_2O_3. Dissolve 20 g. chromium sulphate in 50 c.c. distilled water, or use the chrome alum solution obtained in the preparation of aldehyde (200), heat and add dilute ammonia solution until no more precipitate is obtained. Boil for 15 minutes and allow the precipitate to settle. Decant the clear liquid and wash the precipitate by decantation with boiling water until free from ammonium sulphate. Filter on a fluted filter and dry in the steam oven. Transfer to a crucible or dish, ignite to convert the hydroxide to oxide, and grind to powder in a mortar. A dull green amorphous powder is left, almost insoluble in acids. Chromium sesquioxide is also produced when ammonium dichromate is heated :

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

146. Nickel sesquioxide, Ni_2O_3. Dissolve 10 g. of pure metallic nickel in dilute nitric acid, make up the solution to 250 c.c. with distilled water and filter from any residue. Evaporate to dryness on the steam-bath. Nickel nitrate remains as a green crystalline residue. Transfer to a weighed silica dish. [If pure metal is not available, take 50 g. of pure nickel nitrate, free from cobalt, in the silica dish.] Ignite the nitrate, gently at first, to expel all water of crystallisation, in which the salt melts, and then strongly until no further change occurs and the weight of the residue is constant. Abundant red fumes are evolved and the green nitrate changes to the dark grey oxide.

The oxide dissolves in nitric or sulphuric acid, evolving oxygen, and in hydrochloric acid with evolution of chlorine, and nickelous salts are produced. It is readily reduced, by heating to 200–300° in hydrogen, to form metallic nickel.

Many other oxides can be prepared by this method, as CuO, PbO, BaO, etc.

147. Mercuric oxide, HgO. Dissolve mercury in nitric acid and evaporate to dryness. Mix the residue with about an equal

weight of mercury, and heat in the porcelain dish, in the fume chamber. The temperature should not be more than sufficient to decompose the nitrate. Use a glass rod to stir the mixture and break up the pieces of mercuric nitrate. If the temperature is too high, much of the mercury will volatilise and some of the mercuric oxide will be decomposed. Allow the residue to cool, add water and boil. Filter and wash with hot water to remove undecomposed nitrate. Dry and press through wash leather to remove unaltered mercury. The residue is red.

Mercuric oxide may also be prepared by adding a solution of sodium hydroxide to a solution of a mercuric salt. The precipitate is mercuric oxide, and is yellow. It must be *well* washed with hot water to remove the caustic soda. The residue is dried in an air oven.

148. Cuprous oxide, Cu_2O. (*a*) Mix together 20 g. cuprous chloride and 15 g. dry sodium carbonate, and heat gently in a covered crucible. Cuprous oxide is obtained as a non-crystalline red powder.

$$Cu_2Cl_2 + Na_2CO_3 = Cu_2O + 2NaCl + CO_2.$$

Extract the residue when cold with water, to remove sodium chloride and excess of sodium carbonate, filter, wash till free from chloride, and dry the residue of cuprous oxide.

(*b*) To 500 c.c. of Fehling's solution prepared as in **480**, add 12 g. of glucose in a little water, and warm on a sand-bath until the copper is completely precipitated as cuprous oxide. Allow this to settle, wash by decantation several times with hot water, filter and complete the washing on the filter till free from alkali.

Cuprous oxide dissolves in conc. hydrochloric acid to form cuprous chloride. It is converted by nitric acid into cupric nitrate, with evolution of nitrogen oxides, and by sulphuric acid into a mixture of cupric sulphate and metallic copper.

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

149. Manganous oxide, MnO. Dissolve separately in as little hot water as possible 20 g. manganous sulphate and 12 g. ammonium oxalate. Filter the two solutions if they are not quite

clear, and mix together. Manganous oxalate is precipitated as a pale pink, crystalline powder. Drain on the pump, wash with a very little cold water, and dry on a porous plate. Place this dry powder in a piece of hard glass tube 8–12 inches long, pass a stream of dry carbon dioxide gas, and heat gently with the burner until the oxalate is completely decomposed. Manganous oxide remains as a grey-green powder,

$$MnC_2O_4 = MnO + CO + CO_2,$$

which, on exposure to air, changes to higher oxides. Transfer it, while the carbon dioxide is still passing, to a strong tube closed at one end and then seal the tube.

150. Lead peroxide, PbO_2. Lead hydroxide is precipitated from solutions of lead salts by the addition of alkalis. If the precipitate be acted upon by a suitable oxidising agent, the hydroxide is converted to the peroxide.

(*a*) To a solution of lead acetate add a slight excess of sodium hydroxide solution and then add hydrogen peroxide and warm. A brown precipitate of the peroxide is produced.

Sodium peroxide can be used instead of sodium hydroxide and hydrogen peroxide.

Bleaching powder acts simultaneously as an alkali and as an oxidising agent and can be used for the preparation of the peroxide.

(*b*) * Dissolve 50 g. crystallised lead acetate in 200 c.c. water in a large flask or porcelain dish and heat on the steam pan. Grind up 100 g. good bleaching powder with water, make up to 1,500 c.c., shake well, and allow to settle. Filter the supernatant liquid and add it slowly to the hot solution of lead acetate, with constant stirring or shaking, until a filtered test portion gives no more brown precipitate on boiling with more of the bleaching powder. Continue heating for some time until the precipitated lead peroxide is dark brown in colour. Wash by decantation with hot water until the washings are free from chloride, drain on the pump and dry in the steam oven, or keep the peroxide as a paste under water. Yield, 25–30 g.

* Gattermann, *Practical Methods of Organic Chemistry*.

Red lead may be regarded as a basic lead plumbate, $(PbO)_2 . PbO_2$, and when warmed with nitric acid, the basic oxide is converted to the nitrate and the acidic oxide is liberated.

(*c*) Mix 60 c.c. conc. nitric acid with 250 c.c. water in a porcelain dish, warm gently on the steam-bath, and slowly stir in 70 g. red lead made into a paste with water. Two-thirds of the lead dissolves as nitrate, and lead peroxide remains.

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

Heat on the steam-bath, stirring frequently, for half an hour ; allow to settle, decant and wash by decantation as above till no lead can be detected in the washings. Yield, 20–22 g.

From the filtered solution lead nitrate crystallises on cooling.

REDUCTION OF METALLIC OXIDES

151. Many reducing agents may be used for this purpose, such as hydrogen and hydrocarbons, carbon, carbon monoxide, sulphur and hydrogen sulphide. Carbon in some form is the fuel employed in most metallurgical reductions.

The metals nearest to hydrogen in the electrical series (87) are readily obtained from the oxides by heating in hydrogen : Fe, Ni, Co, Pb, Sn, Bi, Cu. The action may be reversible, as in the case of iron, this depending on the temperature, the mass law (67), and the relative heats of formation of the oxide and water :

$$Fe_2O_3 + 3H_2 \rightleftharpoons 2Fe + 3H_2O.$$

Aluminium and magnesium, whose oxidation evolves great heat, can be used to reduce many metallic oxides. It is only necessary to start the reaction at one point in the mixture ; the temperature reached is so high that the molten metal is obtained, covered by a fluid slag of impure aluminium oxide.

Manganese. Prepare about 80 g. of trimanganic tetroxide by strongly heating the dioxide :

$$3MnO_2 = Mn_3O_4 + O_2.$$

Mix the product with the calculated quantity of aluminium powder and pack tightly in a fireclay crucible. To start the action

cover with a thin layer of potassium permanganate and aluminium in equal parts, place a short piece of magnesium ribbon in the centre and light the magnesium. The crucible should be surrounded with sand and as soon as the action is started the lid should be placed on the crucible and more sand put round.

$$8Al + 3Mn_3O_4 = 4Al_2O_3 + 9Mn.$$

When cool break the crucible to obtain the mass of manganese.

A mixture of ferric oxide and aluminium powder, known as " thermit ", produces molten iron at a high temperature. This is used for special alloy steels, for welding iron and steel, and for rails, broken castings and machine parts.

Chromium, nickel and other metals can be made similarly.

PREPARATION OF CARBONATES

152. The carbonates of the metals can be produced :

(*a*) By precipitation, in the case of insoluble carbonates. The usual method is to add a solution of sodium carbonate to a solution of a salt of the metal. Sodium carbonate is, however, hydrolysed to a large extent in solution and produces hydroxyl ions. The precipitate is therefore generally a mixture of hydroxide and normal carbonate, or a basic carbonate.

The bicarbonates of sodium and potassium are solids, easily decomposed by heat or by warming their solutions. Calcium and magnesium bicarbonates are less stable, occurring only in solution. The bicarbonates of other metals are still less stable, and hence if sodium bicarbonate be added to solutions of their salts, the normal carbonates of the metals are precipitated. In some cases the normal carbonate is hydrolysed by the water and the hydroxide is produced, e.g. aluminium.

(*b*) By passing carbon dioxide through a solution of the hydroxide. In this way, the carbonates of sodium, potassium, barium, calcium, etc. can be formed, and as the hydroxides of some metals are very slightly soluble in water it would be possible to produce even their carbonates by this method. The formation of lead carbonate in lead pipes is due to the production of the

slightly soluble lead hydroxide and its precipitation as basic carbonate by the carbonic acid present in the water :

$$Pb + O_2 + 2H_2O = Pb(OH)_2 + H_2O_2.$$
$$3Pb(OH)_2 + 2CO_2 = 2PbCO_3 . Pb(OH)_2 + 2H_2O.$$

153. Sodium bicarbonate, $NaHCO_3$. When carbon dioxide is passed into a solution of sodium hydroxide, the carbonate is formed first. As sodium carbonate gives a strongly alkaline solution it is difficult to determine the point at which the whole of the hydroxide is converted to the normal carbonate. Further passage of the gas will finally produce sodium bicarbonate :

$$NaOH + H_2CO_3 = NaHCO_3 + H_2O.$$

By boiling the solution thus obtained, or by adding to it an amount of sodium hydroxide equal to that used originally, the normal carbonate is produced :

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$
$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O.$$

Sodium bicarbonate, being only slightly soluble in cold water, can be precipitated by adding a saturated solution of ammonium bicarbonate to a saturated solution of common salt.

Dilute 250 c.c. of ·880 ammonia with twice its volume of water and place it in a litre flask. Pass in a steady stream of carbon dioxide till absorption ceases. Keep the flask cool during the operation. If a precipitate forms, add water to dissolve it. Make a saturated solution of 200 g. of common salt in water and add to it the solution of ammonium bicarbonate till no further precipitation is observed. Keep the solution cool during the addition. Filter, wash the precipitate with small amounts of cold water to remove the ammonium chloride, and dry in a steam oven.

$$NH_3 + H_2O + CO_2 = NH_4HCO_3.$$
$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

Compare this method with the Solvay or Ammonia Soda process. See also the preparation of ammonium sulphate (160).

The solubility of sodium bicarbonate is 9·8 at 20°, that of the normal carbonate being 21·4.

154. Sodium hydroxide, NaOH, was formerly obtained by boiling sodium carbonate with milk of lime. It is now manufactured by the electrolysis of brine, when the metal liberated at the cathode forms caustic soda and hydrogen. It is of great importance, being used in hard soap manufacture, in purifying cellulose for artificial silk, in the mercerisation of cotton, in the extraction of phenol from the carbolic oil fraction of coal tar, and in many alkali fusions in organic chemistry (285, 289).

PREPARATION OF SULPHITES

155. Sulphites and bisulphites can be produced by passing sulphur dioxide into solutions of hydroxides (compare **152**).

Sulphur dioxide is much more soluble in water than carbon dioxide and also forms a stronger acid. The carbonates therefore can be used instead of the hydroxides. Further, since when the gas is passed through a solution of sodium carbonate, the liberated carbon dioxide is swept out, the whole of the sodium carbonate is converted to sulphite and then to bisulphite.

156. Sodium sulphite, $Na_2SO_3 . 7H_2O$. Dissolve 30 g. crystallised sodium carbonate in 100 c.c. of water, and divide the solution into two equal parts. Saturate one half with sulphur dioxide. Carbon dioxide is expelled and sodium bisulphite produced.

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

Now add the other half of the sodium carbonate solution. More carbon dioxide gas is evolved, and sodium sulphite formed.

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + CO_2 + H_2O.$$

The sulphite crystallises in transparent monoclinic prisms, which are efflorescent. Above 22° the anhydrous salt separates. It is used as a mild bleach for wool and silk, as an antichlor, and in photographic developers.

157. Sodium hydrogen sulphite, $NaHSO_3$, is formed in the first stage in the above experiment. It may be crystallised by evapor-

ation at low temperatures. Solid sodium bisulphite is largely the metabisulphite, $Na_2S_2O_5$, which forms anhydrous prisms in the cold.

The hot solution of bisulphite is used in the purification of wood pulp for paper-making, as it dissolves gums and resins without affecting the cellulose. It is used also in preserving food and grain, and in sterilising brewery casks.

158. Sodium thiosulphate, $Na_2S_2O_3 . 5H_2O$. Prepare sodium sulphite as above from 25 g. sodium carbonate, or dissolve 25 g. sodium sulphite in 100 c.c. water, and add 5 g. flowers of sulphur. Boil gently for about half an hour until the alkaline reaction of the sulphite has disappeared, and filter. Sodium thiosulphate is produced by the union of sulphur with the sulphite,

$$Na_2SO_3 + S = Na_2S_2O_3,$$

and crystallises from the filtrate in large transparent monoclinic prisms, containing five molecules of water.

It was formerly obtained by oxidation of the alkali waste (CaS) of the old Leblanc process. It is now produced by absorbing sulphur dioxide from sulphur or pyrites burners in the waste liquors from sodium sulphide manufacture :

$$2Na_2S + Na_2CO_3 + 4SO_2 = 3Na_2S_2O_3 + CO_2.$$

The salt is unchanged in air, and the solution is neutral. When a dilute solution is acidified, no immediate change is apparent, but soon pale yellow sulphur is precipitated from the unstable thiosulphuric acid :

$$H_2S_2O_3 = H_2O + SO_2 + S.$$

Sodium thiosulphate reacts with halogens, and is largely used for the estimation of free iodine and as an antichlor in the bleaching of paper pulp, calico, etc.

$$2Na_2S_2O_3 + I_2 = 2NaI + \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6}.$$

The solution of thiosulphate also dissolves silver halides and is employed as a fixing agent in photography, usually under the erroneous name of " hyposulphite " or " hypo ".

$$Na_2S_2O_3 + AgCl = NaCl + AgNaS_2O_3.$$

159. Barium dithionate, $BaS_2O_6 . 2H_2O$. 20 g. of finely powdered manganese dioxide are suspended in water and sulphur dioxide is passed in, with frequent shaking, until no more of the oxide will dissolve. The solution contains manganese dithionate and a small quantity of sulphate.

$$MnO_2 + 2SO_2 = MnS_2O_6.$$

$$MnO_2 + MnS_2O_6 = 2MnSO_4.$$

The manganese salt may be obtained in easily soluble rhombohedral crystals, with three molecules of water, $MnS_2O_6 . 3H_2O$. It is better to prepare the barium salt, which can be obtained from it, quite free from sulphate, by adding a solution of barium hydroxide as long as a precipitate forms.

$$MnS_2O_6 + Ba(OH)_2 = BaS_2O_6 + Mn(OH)_2.$$

$$MnSO_4 + Ba(OH)_2 = BaSO_4 + Mn(OH)_2.$$

Warm gently and filter off the precipitated barium sulphate and manganese hydroxide. Barium dithionate may then be crystallised from the filtrate by slow evaporation in a warm place. It forms colourless, transparent rhombic prisms.

On heating dithionates in a dry tube, or on boiling the aqueous solution for some time, especially in presence of a little hydrochloric acid, they are all decomposed into sulphur dioxide and the sulphate.

$$BaS_2O_6 = BaSO_4 + SO_2.$$

Note for student. Devise a scheme to distinguish between sulphites, bisulphites, thiosulphates, sulphates, and dithionates.

PREPARATION OF SULPHATES

Sulphuric acid is made either by the chamber process or the contact process. Sulphates can be made by methods indicated for chlorides in par. 128.

160. Ammonium sulphate, $(NH_4)_2SO_4$. This important salt, used chiefly as a fertiliser, was, and to some extent still is, made by passing ammonia into 50 per cent. sulphuric acid and centrifuging the crystals to remove the mother liquor.

Ammonium sulphate is now made by a process similar to that used for the manufacture of sodium bicarbonate by the ammonia soda process (153).

Pour 50 c.c. of ·880 ammonia into a 500 c.c. flask, dilute to 150 c.c. and add 60 g. of calcium sulphate. Pass carbon dioxide through the mixture for about two hours, boil the product for a few minutes and filter. Concentrate the filtrate and allow to crystallise or evaporate it to dryness.

The solubility of calcium carbonate is much less than that of calcium sulphate and therefore ammonium sulphate is formed in solution :

$$2NH_3 + H_2O + CO_2 = (NH_4)_2CO_3.$$
$$CaSO_4 + (NH_4)_2CO_3 = CaCO_3 + (NH_4)_2SO_4.$$

161. Magnesium sulphate, $MgSO_4 . 7H_2O$ (Epsom Salt). Neutralise 50 c.c. of dilute sulphuric acid with magnesium carbonate, heat nearly to boiling and filter at once. Magnesium sulphate crystallises from the filtrate in four-sided rhombic prisms containing seven molecules of water of crystallisation. When heated, the crystals melt in this water, and lose six molecules at 150°, the seventh at 200°. The crystals are isomorphous with the corresponding sulphates of zinc, iron, nickel, etc.

Epsom salt is used in medicine as a purgative, and is also employed in dressing and weighting cotton goods, and as a mordant in dyeing.

162. Copper sulphate, $CuSO_4 . 5H_2O$ (Blue Vitriol). Neutralise 50 c.c. of dilute sulphuric acid by boiling with copper oxide, or by adding copper carbonate. The blue filtered solution deposits copper sulphate on cooling, in transparent, blue triclinic crystals containing five molecules of water. Four of these are lost at 100°, the fifth at 220–230°. Copper sulphate is used as a mordant in calico-printing, and in dyeing, in making certain pigments, as Scheele's green and emerald green, and in the electrometallurgy of copper.

163. Purification of copper sulphate. The commercial copper sulphate contains some iron. Dissolve 200 g. in 300 c.c. of hot

water, add 12 g. of lead peroxide and boil for an hour, keeping a constant bulk of liquid by addition of water. Add a little barium carbonate and stir well, keeping the solution warm.

Test a few c.c. as follows. Filter, add ammonium hydroxide in excess and filter again. Wash the filter paper ; if a brown precipitate is seen iron is present.

Oxidise the original substance further with lead peroxide, add more barium carbonate if necessary and again test. If free from iron, filter the whole of the liquid, concentrate and crystallise.

164. Zinc sulphate, $ZnSO_4 . 7H_2O$ (White Vitriol). The solution from the hydrogen generator may be used, excess of zinc being added to render the solution as nearly neutral as possible and to prevent the solution of arsenic and lead which may be present as impurities. Filter the supernatant liquid through an asbestos filter. Oxidise any iron present by passing chlorine through the solution. The iron should not be precipitated with ammonium hydroxide owing to the formation of ammonium sulphate which will crystallise with the zinc sulphate. It may be precipitated by boiling with a small quantity of zinc carbonate (which may be prepared by precipitating a small portion of the solution with sodium carbonate, filtering and washing the precipitate), stirring during the heating.

Test the clear liquid with potassium thiocyanate for iron, and if free, filter through asbestos and evaporate the filtrate till saturated. Allow the solution to crystallise. Press the crystals between layers of filter paper and dry at a low temperature.

Zinc sulphate crystallises in long rhombic prisms which are efflorescent. At 100° it parts with 6 molecules of water of crystallisation, and with the last molecule at 300°. It decomposes on heating strongly, forming zinc oxide. It is used in medicine and in dyeing and printing.

165. Potassium dichromate, $K_2Cr_2O_7$. Take 30 g. of finely powdered chromite, or chromium sesquioxide, Cr_2O_3, and mix well by grinding in a mortar with 30 g. powdered potassium nitrate and 20 g. dry potassium carbonate. Place the mixture in a

large earthenware crucible and heat to redness in a muffle furnace for several hours. Allow to cool and extract the yellow mass with boiling water. Filter from oxide of iron and concentrate the solution.

$$2Cr_2O_3 . FeO + 4K_2O + 7O = 4K_2CrO_4 + Fe_2O_3.$$

Add sulphuric acid till the solution is strongly acid. The chromate is converted into dichromate, which crystallises readily. Filter the crystals at the pump, using a plug of asbestos or glass wool instead of paper, wash with a little cold water, and concentrate the filtrate. The later separations are liable to contain potassium sulphate. Recrystallise the dichromate from hot water. It crystallises in anhydrous orange-red triclinic prisms, which melt without decomposition below a red heat and decompose at higher temperature into oxygen, chromium sesquioxide and the normal potassium chromate.

Potassium dichromate is largely used in dyeing and calico-printing, as an oxidising agent, and in the preparation of other chromium compounds. The solution has an acid reaction, and is poisonous.

166. Potassium chromate, K_2CrO_4. Dissolve 30 g. potassium dichromate in 100 c.c. water, and add slowly to the warm solution 14 g. dry potassium carbonate. The normal chromate is produced :

$$K_2Cr_2O_7 + K_2CO_3 = 2K_2CrO_4 + CO_2.$$

Boil the liquid to expel carbon dioxide, filter and evaporate. The salt crystallises in yellow rhombic pyramids and is very soluble in water, but insoluble in alcohol. The solution has a strong yellow colour and an alkaline reaction. When heated the salt becomes darker in colour and melts at a high temperature without decomposition.

167. Chromium trioxide, CrO_3 (Chromic Anhydride). Dissolve 60 g. of potassium dichromate in 100 c.c. water, and add 85 c.c. conc. sulphuric acid. Allow the mixture to stand overnight in a cool place, when potassium bisulphate will crystallise out. Decant the liquid, heat the mother liquor to 80–90° and add

30 c.c. conc. sulphuric acid. If a precipitate of chromium trioxide separates, add water till it just redissolves. Evaporate over steam until crystals begin to form in the liquid, and set aside for a day. Decant the liquor and evaporate to obtain a further crop. Drain the crystals on a funnel loosely plugged with glass wool, using the pump, and wash twice with small quantities of conc. nitric acid to remove sulphuric acid and sulphates. Place in a porcelain dish and dry by heating very gently on a sand-bath.

Chromium trioxide crystallises in long rhombic prisms of a deep crimson colour. It melts unchanged at 195°, forming a deep-red liquid, and at 250° decomposes into oxygen and the sesquioxide. It is a powerful oxidising agent.

168. Lead chromate, $PbCrO_4$ (Chrome Yellow). Dissolve 100 g. of lead acetate or lead nitrate in water. Calculate the necessary quantity of potassium chromate or of sodium chromate and dissolve in water. Filter the solutions, mix the clear liquids and stir well. Wash the precipitate well by decantation, testing the supernatant liquid for lead and chromate. When free from these pour off the liquid and filter through a fluted filter or cloth filter. Press out as much water as possible, break up and dry in the steam oven.

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3.$$

The precipitate is chrome yellow and may be obtained in lighter shades by replacing a portion of the potassium chromate with sodium sulphate, when lead sulphate will be precipitated with the chromate.

169. Basic salts. Acid salts can be made by adding excess of a polybasic acid to a base (153). Similarly, basic salts can be made by the action of excess of a polyacidic base on an acid. As an example, aluminium sulphate solution when boiled with aluminium hydroxide will give a basic sulphate. The more general method is to remove a portion of the anion from the normal salt by means of another base. Hydrolysis of the salt of a weak base and a strong acid is an example of this. If the basic salt formed is insoluble in water, it is precipitated and further action occurs.

Bismuth, tin, iron, copper and many other metals form basic salts in this way :

$$Sn^{\cdot\cdot} + 2Cl' + H^{\cdot} + OH' \rightleftharpoons Sn(OH)Cl + H^{\cdot} + Cl'.$$

The solution becomes acid. If such a basic salt be washed for a long time with water it will in some cases pass completely to the base. An increase in the concentration of the hydroxyl ions brings about more rapid precipitation of the basic salt, though a large concentration may give the base. Thus the addition of a strong base may give the basic salt, or the base itself may be precipitated.

Basic lead chromate (Chrome Red). Take a portion of the chrome yellow before drying and boil with dilute caustic soda solution. The yellow colour will change to orange or red owing to the formation of basic chromate of lead.

$$2PbCrO_4 + 2NaOH = PbCrO_4 \,.\, Pb(OH)_2 + Na_2CrO_4.$$

These chromates are used as pigments.

170. Potassium permanganate, $KMnO_4$. Place 70 g. caustic potash and 30 g. potassium chlorate in a deep iron sand tray, add 50 c.c. water and warm until all is dissolved. Stir in 60 g. finely-powdered pyrolusite, and evaporate with constant stirring until the paste solidifies. Cover with another dish and heat to dull redness until the mass is quite hard and dry. Allow to cool, break up and powder the dark green or brown mass of potassium manganate, and boil in $1\frac{1}{2}$ l. of water for an hour, while passing a stream of carbon dioxide gas. A heavy precipitate of manganese dioxide is formed. Continue this until the liquid is violet in colour. The manganate is now changed to permanganate.

$$3MnO_2 + KClO_3 + 6KOH = 3K_2MnO_4 + KCl + 3H_2O.$$

$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + 2K_2CO_3 + MnO_2.$$

Allow the precipitate to settle, decant through a glass-wool filter, wash the precipitate twice with boiling water, and concentrate the combined filtrates. Allow to cool in a covered dish and avoid all contact with dust, organic matter, or reducing gases.

Potassium permanganate crystallises in dark violet rhombic prisms, with a green metallic lustre. The crystals are isomorphous with potassium perchlorate. Heated alone, they decompose into oxygen, manganese dioxide, and potassium manganate which is also further decomposed. The substance is largely used as an oxidising agent in the laboratory, and as a disinfectant.

PREPARATION OF NITRATES

Nitrates can be prepared by the general methods for the preparation of salts (128).

171. Ammonium nitrate, NH_4NO_3, may be prepared by neutralising nitric acid with ammonium hydroxide, and evaporating the solution to the crystallising point :

$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O.$$

A brown sediment due to traces of iron and tarry matter from the ammonia may appear during the evaporation, and should be filtered. The salt may be used for preparing nitrous oxide.

Ammonium nitrate was manufactured in large quantities during the war of 1914–18 by mixing the sulphate with sodium nitrate ; sodium sulphate separates from the hot solution, and ammonium nitrate on cooling :

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3.$$

This was mixed with T.N.T. (247) to secure complete combustion of the explosive (amatol) on detonation.

172. Lead nitrate, $Pb(NO_3)_2$. Place 25 g. of litharge in an evaporating dish and add water, stir and add nitric acid in small portions till all the litharge is dissolved, keeping the solution hot during the experiment, and the bulk of liquid constant by addition of water. Evaporate to dryness on the water-bath. Dissolve in water, filter, add a few c.c. of nitric acid, evaporate till concentrated and allow to crystallise.

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Lead nitrate crystallises in regular octahedra, and has a solubility of 50 at ordinary temperatures.

173. Sodium nitrite, $NaNO_2$, was formerly prepared by fusing the nitrate with reducing agents such as lead, carbon, sulphur or sulphides. The lead process was laborious and unhealthy, and is now obsolete. The substance is now obtained by dissolving a mixture of nitrogen oxides got by the catalytic oxidation of synthetic ammonia, or by the Birkeland-Eyde process from air, in sodium hydroxide solution :

$$NO + NO_2 + 2NaOH = 2NaNO_2 + H_2O ;$$

this gives a very pure product.

Sodium nitrite crystallises in deliquescent prisms. It is soluble in an equal weight of water at room temperature, with great heat absorption. It is largely used in preparing azo-dyes, and in dyeing.

174. Hydroxylamine sulphate, $(NH_2OH)_2 . H_2SO_4$.* Dissolve 75 g. sodium nitrite and 140 g. crystallised sodium carbonate in as little ice water as possible, and pass in sulphur dioxide until the solution is just acid, stirring well and keeping the liquid at 2–3° below zero by immersion in ice and brine. The nitrite is completely converted at this temperature into sodium hydroximinosulphonate.

$$NaNO_2 + Na_2CO_3 + 3SO_2 + H_2O = HO . N(SO_3Na)_2 + NaHSO_3 + CO_2.$$

Add a few drops of sulphuric acid ; the temperature rises, owing to hydrolysis of the hydroximinosulphonate into hydroxaminosulphonate.

$$HO . N(SO_3Na)_2 + H_2O = HO . NH(SO_3Na) + NaHSO_4.$$

Heat slowly to 90°, and keep the solution at 90–95° for two days, to complete the hydrolysis into hydroxylamine sulphate.

$$HO . NH(SO_3Na) + H_2O = NH_2 . OH + NaHSO_4.$$

The liquid must not be boiled, or much of the hydroxylamine will be destroyed. To ascertain whether the change is complete, add excess of barium chloride to a small portion of the liquid, filter, and boil the filtrate with a crystal of potassium chlorate, to convert any sulphonate into sulphate. If no further precipitate is obtained, the hydrolysis is complete.

* Divers and Haga, *J.C.S.* (1896), 1665.

Now neutralise the solution with sodium carbonate, using methyl orange as indicator, and evaporate till the liquid weighs 790–820 g. Cool to 0° or −5°, when nearly all the sodium sulphate will crystallise out. Filter, wash the crushed crystals with a little ice water, and evaporate until the liquor, on cooling to the room temperature, gives a large quantity of hydroxylamine sulphate. Evaporate the mother liquor carefully, separate sodium sulphate as before and then obtain more hydroxylamine sulphate. Purify the latter by recrystallisation. Yield of crude hydroxylamine sulphate, about 60 g.

The salt forms large, non-deliquescent crystals, soluble in three-quarters of its weight of water at 20°. The free base is alkaline in reaction, and is a strong reducing agent, precipitating gold and mercury from solutions of their salts and cuprous oxide from cupric salts.

175. Cuprammonium sulphate, $CuSO_4 . 4NH_3 . H_2O$. When ammonia is added to a solution of copper sulphate, a pale blue basic sulphate is first precipitated, which dissolves in excess of ammonia to form a dark blue solution, containing the above salt. To obtain this in crystalline form, prepare a concentrated solution by adding a slight excess of ·880 ammonia to a saturated solution of copper sulphate. When the solution is clear, cover it with an equal bulk of alcohol added carefully from a pipette or tap funnel. The salt is deposited in long, thin, blue rhombic prisms, which on exposure to air lose ammonia, and change into ammonium sulphate and basic copper sulphate. When heated gently to 150°, the crystals decompose to an apple green powder of the composition $CuSO_4 . 2NH_3$.

The blue solution contains a complex cupri-ammonium ion, from which the copper may be precipitated by sulphuretted hydrogen, but not by caustic alkali.

176. Antimony trichloride, $SbCl_3$. Place 50 c.c. of concentrated hydrochloric acid in a porcelain dish and add in small portions 30 g. of antimony trioxide, stirring during the addition. Heat gently and then boil till excess of acid is driven off and a drop of

the liquid solidifies on cooling. Transfer to a retort fitted with a thermometer and distil. When the temperature reaches 200° collect the antimony trichloride in a dry receiver.

$$Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O.$$

Antimony trichloride is a deliquescent white crystalline substance, melting at 72° and boiling at 223°. It decomposes in water, but dissolves in alcohol unchanged. It is known as "butter of antimony". It may be crystallised from carbon disulphide.

177. **Silicic acid and pure silica.** In a dry half-litre flask fitted with thistle funnel and delivery tube place a mixture of 20 g. of fine sand and 25 g. of powdered fluor spar. Allow the delivery tube to dip just below the surface of mercury (about 1 in. deep) contained in a gas jar. Have the delivery tube perfectly dry. Pour water (6 in. deep) on the surface of the mercury. Down the thistle funnel pour conc. sulphuric acid and shake the flask to moisten the whole mass. (If any of the mixture at the bottom of the flask remains dry, the flask will probably crack on heating.) Heat the flask on a sand-bath. Silicon tetrafluoride is given off, and bubbling through the mercury is decomposed by the water, forming a precipitate of silicic acid and leaving in solution hydrofluosilicic acid. Filter, dry the precipitated silica gel and heat strongly. Pure silica is left. The filtrate may be used for the preparation of barium fluosilicate.

$$2CaF_2 + 2H_2SO_4 = 2CaSO_4 + 4HF,$$

$$4HF + SiO_2 = SiF_4 + 2H_2O,$$

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6,$$

$$H_4SiO_4 = 2H_2O + SiO_2.$$

PREPARATION OF SULPHIDES

Most sulphides can be prepared by direct union of the elements (126). When sulphuretted hydrogen is passed into a solution of an alkali hydroxide the sulphide is first formed and then the bisulphide (hydrosulphide). Insoluble sulphides can be prepared

by precipitation from solutions of salts by the passage of sulphuretted hydrogen or the addition of a solution of a soluble sulphide. Some sulphides, such as those of aluminium and chromium, are hydrolysed readily and give the hydroxide (93).

178. Alkali sulphides. Sodium sulphide, $Na_2S \cdot 9H_2O$, crystallises from concentrated solutions obtained by absorbing waste H_2S in caustic soda. The crystals lose water above 48·9° C., forming lower hydrates. The salt is hydrolysed on warming the solution :

$$Na_2S + H_2O \rightleftharpoons NaSH + NaOH.$$

It is largely used in dyeing and tanning.

Ammonium sulphide, $(NH_4)_2S$, is prepared by absorbing H_2S in ammonium hydroxide. The solid cannot be obtained from this solution owing to dissociation, but a mixture of the two gases at −18° C. deposits it in colourless crystals, which decompose at room temperature into ammonia and the hydrosulphide :

$$(NH_4)_2S \rightleftharpoons NH_4SH + NH_3.$$

For use as a reagent it is usual to pass sulphuretted hydrogen through the ammoniacal solution.

179. Yellow ammonium sulphide, $(NH_4)_2S_{1+x}$. Ammonium sulphide solution decomposes on standing, liberating sulphur, which dissolves in the solution forming yellow polysulphides. These may be obtained by allowing the liquid to percolate through sulphur, or by shaking the mixture and filtering :

$$(NH_4)_2S + xS \quad (NH_4)_2S_{1+x}.$$

Acids decompose these, liberating sulphur :

$$(NH_4)_2S_{1+x} + 2HCl = 2NH_4Cl + H_2S + xS.$$

The value of x varies with concentration and other conditions. The compound $(NH_4)_2S_9$ has been prepared, as well as lower persulphides.

Yellow ammonium sulphide is used as a solvent to remove the sulphides of arsenic, antimony and tin from those of the other metals of the copper group (93, 358).

Yellow polysulphides of like properties are obtained similarly from the fixed alkalis and alkaline earths.

180. Cadmium sulphide, CdS (Cadmium yellow). Dissolve 5 g. of cadmium sulphate or chloride in 100 c.c. of water and pass sulphuretted hydrogen through the solution until no further precipitate is obtained. Wash well and dry in the steam oven. The acid liberated in the reaction should not exceed 0·5N.

$$CdSO_4 + H_2S \rightleftharpoons CdS + H_2SO_4.$$

The sulphide is used as a permanent yellow pigment of a beautiful shade, which becomes deeper as the concentration of acid increases in the solution in which the sulphide is precipitated.

181. Phosphoric acid, H_3PO_4. Place 10 g. of red phosphorus in a porcelain dish, cover with water and add concentrated nitric acid of equal bulk. Place in the fume cupboard and warm gently. Copious red fumes will be evolved. When the action moderates add nitric acid, if necessary, in small quantities till all oxidation ceases. Heat to drive off excess of nitric acid, dilute the syrupy liquid with water, filter and evaporate till the temperature reaches 200°. About 25 g. of syrup of sp. gr. 1·85 will be obtained.

182. Sodium phosphates. Phosphoric acid is tribasic ; it forms three classes of salts. The disodium salt is used as a laboratory reagent. It is only slightly alkaline and therefore the main products of its ionisation must be Na ions and HPO_4 ions :

$$Na_2HPO_4 \rightleftharpoons 2Na^{\cdot} + HPO_4'',$$

and the alkalinity is due to a small concentration of OH ions, thus :

$$HPO_4'' + H_2O \rightleftharpoons H_2PO_4' + OH'.$$

It follows that NaH_2PO_4 must ionise chiefly as :

$$NaH_2PO_4 \rightleftharpoons Na^{\cdot} + H^{\cdot} + HPO_4'',$$

and the solution will be acid.

The normal salt will be strongly alkaline :

$$Na_3PO_4 + H_2O \rightleftharpoons 3Na^{\cdot} + HPO_4'' + OH',$$

and to a slight extent

$$HPO_4'' + H_2O \rightleftharpoons H_2PO_4' + OH'.$$

Disodium hydrogen phosphate, $Na_2HPO_4 . 12H_2O$. Add sodium hydroxide to a solution of phosphoric acid till the solution is just alkaline to litmus. Concentrate the solution and allow to crystallise.

Monosodium hydrogen phosphate, $NaH_2PO_4 . 4H_2O$. Divide a solution of phosphoric acid into two equal parts. Make one part just alkaline to litmus and add the other part.

Trisodium phosphate, $Na_3PO_4 . 12H_2O$. Noting the volume of sodium hydroxide required to make a solution of phosphoric acid just alkaline, add half as much more of the sodium hydroxide solution.

The disodium salt crystallises in large monoclinic prisms which are efflorescent. When heated, sodium pyrophosphate is obtained:

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

The monosodium salt forms large rhombic crystals. When heated to 204° it gives sodium hydrogen pyrophosphate

$$2NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O,$$

and at 240° loses the remainder of its water to form sodium metaphosphate:

$$Na_2H_2P_2O_7 = 2NaPO_3 + H_2O.$$

The trisodium phosphate crystallises in six-sided prisms.

183. Microcosmic salt (Salt of Phosphorus),

$$Na(NH_4)HPO_4 . 4H_2O.$$

Calculate molecular proportions of sodium phosphate crystals and ammonium chloride to make 100 g. of the mixture. Dissolve the sodium phosphate by adding it in portions to 100 c.c. of boiling water in a flask which should be shaken during solution. Add the ammonium chloride, dissolve, filter if necessary and allow to crystallise. By fractional crystallisation free the substance from sodium chloride.

$$Na_2HPO_4 + NH_4Cl = Na(NH_4)HPO_4 + NaCl.$$

Microcosmic salt is efflorescent. It decomposes at 316° leaving sodium metaphosphate, which unites with metallic oxides forming orthophosphates, some of which are coloured; it is therefore used as a dry test for metals (353):

$$Na(NH_4)HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$
$$NaPO_3 + CuO \rightarrow \underset{\text{(blue bead)}}{CuNaPO_4}.$$

Silica is insoluble in a metaphosphate bead (348):

$$CaSiO_3 + NaPO_3 \rightarrow CaNaPO_4 + SiO_2.$$

184. **Arsenic acid, H_3AsO_4.** In a half-litre retort place 50 g. arsenious oxide in small lumps, and 50 c.c. conc. nitric acid. Direct the retort neck upwards to act as a reflux condenser (Fig. 54), and connect the end by means of a glass tube with a small flask immersed in ice water, in which the nitrous fumes may be condensed. Heat the retort gently on a sand-bath until no more fumes are evolved. Pour off the liquid, evaporate to dryness and test the residue for arsenious acid. If present add aqua regia and again evaporate to dryness until free from arsenious acid. Dissolve in hot water and again evaporate to dryness to expel nitric acid. The residue can then be crystallised from a little hot water. It forms transparent crystals having the formula $2H_3AsO_4 . H_2O$. These melt at 100°, giving off the water of crystallisation, and leaving a white crystalline powder of ortho-arsenic acid, H_3AsO_4.

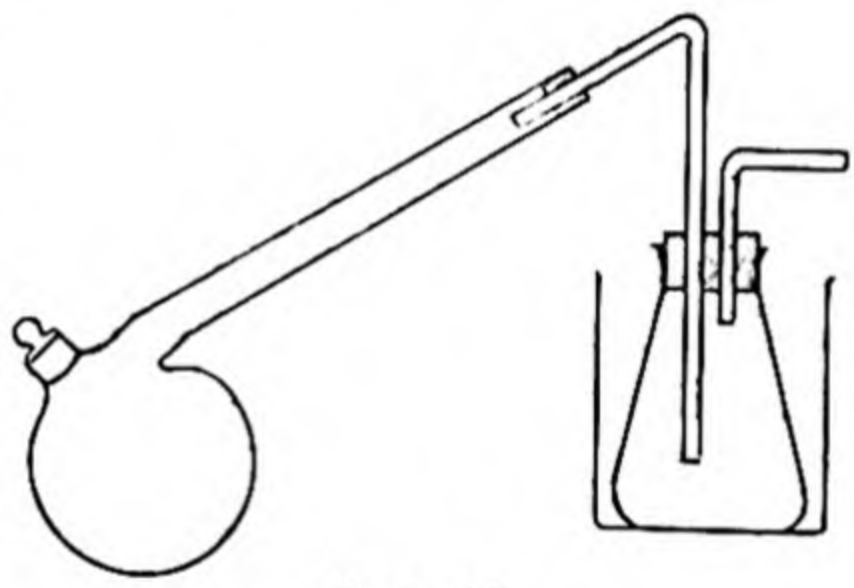


FIG. 54.

Examine the dark-blue liquid which has condensed in the small flask. It contains nitrogen trioxide and tetroxide. Pour it into cold water, and test the solution for nitrous and nitric acids.

185. **Sodium arsenate, $Na_2HAsO_4 . 12H_2O$.** (*a*) To the arsenic acid obtained in last experiment add a slight excess of sodium

carbonate ; filter, and evaporate the solution at a temperature not exceeding 18°. The crystals obtained have the above composition, are isomorphous with sodium phosphate,

$$Na_2HPO_4 . 12H_2O,$$

and efflorescent. At 20° and higher temperatures the crystals contain only seven molecules of water, and are not efflorescent.

(*b*) Place 20 g. of white arsenic in a porcelain dish, add water, and sodium carbonate solution in slight excess. When all is dissolved, add a solution of 15 g. sodium nitrate, evaporate to dryness and ignite in a clay crucible. Dissolve the residue in water, filter and crystallise as above.

Sodium arsenate is readily soluble in water, and the solution is alkaline. The potassium salt, K_2HAsO_4, does not crystallise. Like the free acid, these are mild oxidising agents.

186. Silver nitrate (from Silver Residues). Add conc. hydrochloric acid to the residues, allow to settle, pour off the clear liquid, filter, wash well and dry. Mix the dry residue with four times its weight of fusion mixture together with half its weight of potassium nitrate and place in a fireclay crucible. Heat strongly in a furnace, pour on to an iron plate and allow to cool. Remove as much carbonate from the button as possible by scraping, and boil the silver with hydrochloric acid to dissolve any remaining carbonate.

Dissolve the silver in nitric acid diluted with half its volume of water. Evaporate to dryness to remove nitric acid, dissolve in distilled water, filter and allow to crystallise.

Silver nitrate forms large colourless rhombic plates which melt at 218° and resolidify on cooling to a white fibrous mass known as lunar caustic. Silver nitrate is used largely in analytical and photographic work, and is also employed in medicine and for marking inks.

187. Sodium cobaltinitrite,* $Na_3Co(NO_2)_6$. Pure sodium nitrite should be employed for the preparation of this substance, which is used as a reagent for the detection of potassium.

* Cunningham and Perkin, *J.C.S.* (1909), 1568.

Dissolve 150 g. of sodium nitrite in 150 c.c. of hot water, and cool to 45–50°. Add 50 g. of cobalt nitrate and stir or shake until all is dissolved. Now add 25 c.c. glacial acetic acid, mix thoroughly by shaking, and allow to stand for half an hour. Filter if necessary from traces of yellow potassium cobaltinitrite, and then aspirate a rapid current of air through the liquid to remove oxides of nitrogen. Add 150 c.c. alcohol (95 per cent.) and shake well at frequent intervals for about an hour. A bulky yellow precipitate of sodium cobaltrinitrite is obtained, which is filtered on a Buchner funnel, washed with 60 per cent. alcohol, finally with 95 per cent., then dried on a porous plate.

The salt when dry is a pale orange-yellow crystalline powder, very soluble in water, but not in alcohol.

Potassium cobaltinitrite, $K_3Co(NO_2)_6$, is obtained as a canary yellow precipitate by adding sodium cobaltinitrite to a solution of a potassium salt. Like the ammonium salt, it is very sparingly soluble in water.

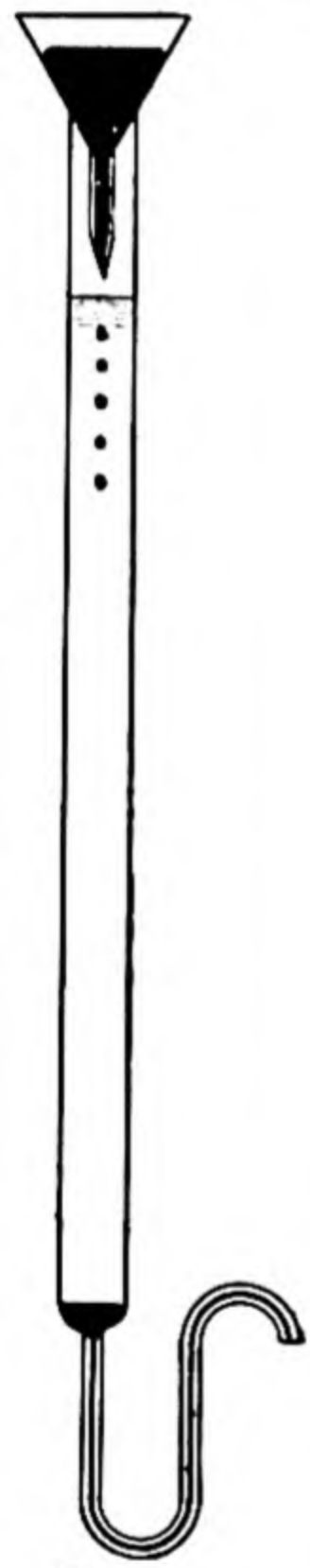


FIG. 55.

188. **Purification of mercury.** Allow the mercury to fall in a succession of small drops from the end of a funnel through a long column of dilute nitric acid of sp. gr. 1·1 (15 per cent. HNO_3, made by mixing 1 part of conc. acid with three of water). Syphon off the acid, wash the mercury several times with water, syphoning off the water, and then dry the mercury, first with filter paper, finally on the steam pan.

A mercury purification tube may also be used (Fig. 55). The bottom is first filled with pure dry mercury, nitric acid is introduced, and the stream of impure mercury started. The process is then automatic, the purified mercury syphoning over into a receiver in which it may be dried by placing in the steam oven. Pure distilled mercury boils at 357°.

CARBON COMPOUNDS

ALCOHOLS (ALKANOLS) $C_nH_{2n+1}OH$.

The saturated monohydric alcohols are derivatives of the paraffin hydrocarbons in which one hydrogen atom in the molecule is replaced by a hydroxyl group. The first two members of the series, methyl alcohol and ethyl alcohol, are of great importance in themselves, as solvents and as sources of many derivatives, and are manufactured in vast quantities by special methods. They are miscible with water in all proportions. Among the higher homologues the solubility in water diminishes with increasing molecular weight. Isomerism first appears with the two forms of propyl alcohol, C_3H_7OH.

189. **Ethyl alcohol** (Ethanol), C_2H_5OH. Alcohol is produced on the large scale chiefly by the fermentation of molasses, the dark-coloured mother liquor which remains after crystallising cane sugar from the aqueous extract of beet or sugar cane. The liquor still contains about 50 per cent. of sugar which cannot be economically recovered. It is therefore fermented, and the alcohol is separated by a continuous distillation process (49).

Large quantities of alcohol are now converted into aldehyde, acetic acid, acetone, etc., for solvent and other purposes.

In the laboratory alcohol may be prepared from glucose. 100 g. of commercial glucose is placed in a flask or bottle, dissolved in 750 c.c. water, and 20 g. of yeast, mixed to a uniform cream with water, then added. Fermentation soon sets in, and proceeds most rapidly about 25°. Attach a delivery tube to the flask and show that the gas evolved is carbon dioxide.

$$C_6H_{12}O_6 = 2C_2H_5 \cdot OH + 2CO_2.$$

When the evolution of gas ceases (arrange to leave overnight), distil the filtered liquid, using a Young or Glinsky fractionating column (Fig. 43). Collect in the first distillation up to 95°. About 75 c.c. of dilute alcohol will be obtained. Redistil this portion and collect up to 85°. This will give about 50 c.c. of alcohol,

which may be further dehydrated by adding a few pieces of quicklime.

Alcohol is a colourless, pleasant-smelling liquid, boiling at 78·4°, and of sp. gr. ·793 at 15°. It mixes with water in all proportions, evolving heat.

REACTIONS. 1. Ethyl alcohol burns with a pale, slightly luminous flame, forming water and carbon dioxide.

2. On mixing with conc. sulphuric acid, ethyl hydrogen sulphate is formed with evolution of heat. On warming, the mixture gives off inflammable vapours (ethylene, ether, etc.).

3. When warmed with conc. sulphuric acid and sodium acetate, ethyl acetate is formed, recognised by its pleasant fruity smell.

$$C_2H_5 . OH + CH_3 . COOH = CH_3 . CO . OC_2H_5 + H_2O.$$

4. Acetaldehyde is produced on warming ethyl alcohol with potassium dichromate and dilute sulphuric acid, and is easily detected by its smell and its property of reducing ammoniacal silver.

$$C_2H_5 . OH + O = CH_3 . CHO + H_2O.$$

5. To an aqueous solution of alcohol add a little iodine solution and then sodium hydroxide until the colour of the iodine is nearly discharged. A pale yellow crystalline precipitate of iodoform is thrown down. Note the odour (distinction from methyl alcohol).

$$CH_3CH_2OH + 5I_2 + 7NaOH = CHI_3 + 7NaI + CO_2 + 6H_2O.$$

190. Methyl alcohol (Methanol), $CH_3 . OH$, is obtained in the distillation of wood to the extent of about one per cent., and is the chief constituent of wood spirit. The pure alcohol is a mobile colourless liquid ; b.p. 64·6° : sp. gr. ·796 at 20°. It is miscible with water, and in general properties resembles ordinary alcohol, but it does not give the iodoform reaction. Commercial wood spirit contains a little acetone, which does give iodoform.

Methanol is now manufactured by the Patart process, in which water gas, with additional hydrogen, is passed over a catalyst of metallic oxides (Zn, Cu, Cr) at 350°–400° C. and 300–600 atmospheres : other reactions also may occur, with formation of CH_2O,

CH_4, CO_2 ; but methanol formation involves the largest decrease in volume and is therefore favoured by high pressure (70).

$$CO \xrightarrow[H_2]{} CH_2O \xrightarrow[H_2]{} CH_3OH \xrightarrow[H_2]{} CH_4 + H_2O$$

It is also produced in large quantities by the catalytic oxidation of natural gas (90 per cent. methane).

REACTIONS. 1. Methyl alcohol is readily oxidised on heating with potassium dichromate and sulphuric acid, giving formaldehyde and formic acid.

$$CH_3OH + O = H\,.\,CHO + H_2O.$$

$$H\,.\,CHO + O = H\,.\,COOH.$$

The formic acid may be distilled and detected as under (205).

2. To a little methyl alcohol add some salicylic acid and conc. sulphuric acid and warm gently. Methyl salicylate (oil of wintergreen) is produced.

3. Methyl alcohol rapidly decolorises permanganate; ethyl alcohol does so only slowly.

ALKYL HALIDES, $C_nH_{2n+1}X$

General methods of preparation :

(*a*) Direct substitution in the paraffin,

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

(*b*) The action of the halogen acid on the alcohol,

$$C_2H_5OH + HBr = C_2H_5Br + H_2O.$$

(*c*) The action of a phosphorus halide on the alcohol,

$$3C_2H_5OH + PI_3 = 3C_2H_5I + H_3PO_3.$$

191. Ethyl bromide, C_2H_5Br. The most convenient method for the preparation of ethyl bromide is to distil a mixture of alcohol and potassium or sodium bromide with sulphuric acid.

$$C_2H_5OH + HBr = C_2H_5Br + H_2O.$$

In a half-litre distilling flask (Fig. 56) place 25 g. (30 c.c.) alcohol and 50 g. (28 c.c.) conc. sulphuric acid. Mix well and cool

under the tap. Then add 50 g. coarsely powdered potassium bromide, and warm gently on a sand-bath. Ethyl bromide distils and is condensed in a long condenser, on the end of which is placed an adapter, which dips just under the surface of water in the receiver. The oily drops of ethyl bromide sink to the bottom of this water, and when no more oil is obtained the operation is finished. Transfer the contents of the receiver to a separating funnel, wash the bromide with dilute sodium carbonate solution, then with water, and place in a dry, well-corked flask with a little anhydrous calcium chloride or sodium sulphate. After standing

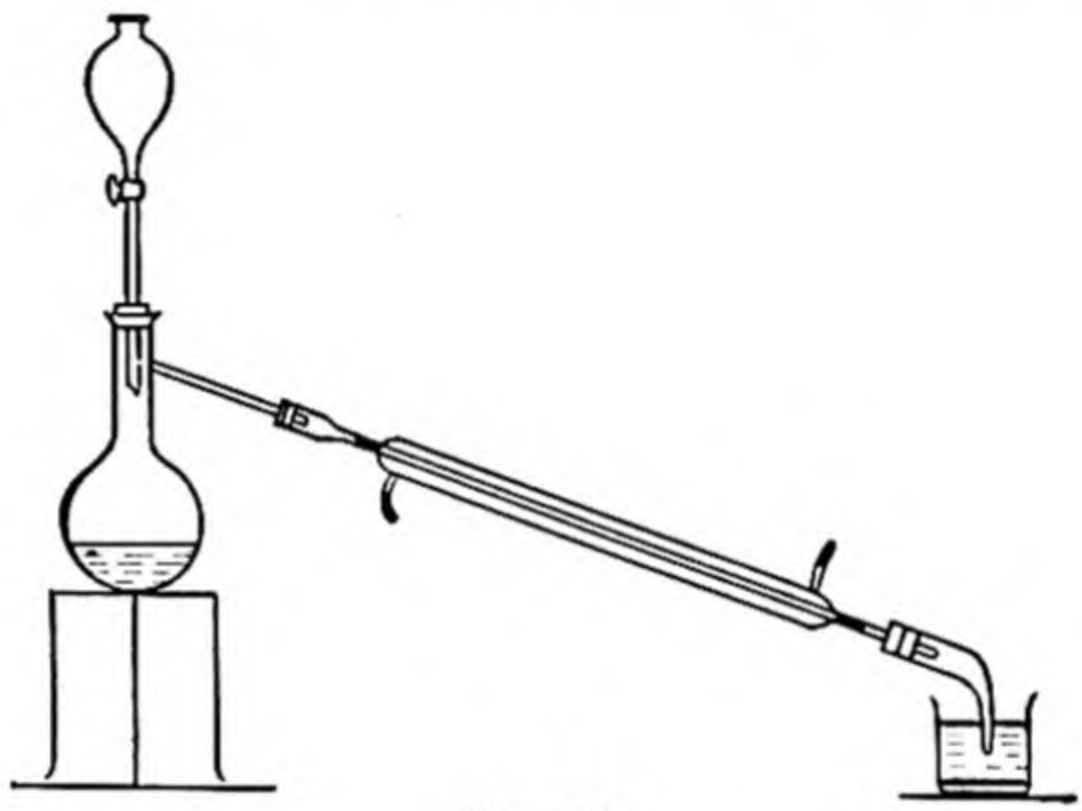


FIG. 56.

overnight, or for at least six hours, decant or filter into a small distilling flask and distil over a small naked flame, placing a few chips of porous plate in the liquid. Collect as ethyl bromide the fraction boiling at 35–40°. Yield 40 g.

Ethyl bromide is a colourless, ethereal smelling liquid, insoluble in water, but miscible with alcohol and ether in any proportion. B.p. 38·8°; sp. gr. 1·47 at 15°.

192. Ethyl iodide, C_2H_5I. Alkyl iodides are usually prepared by the interaction of alcohols with iodine and phosphorus. The usual method is to add the iodine slowly to a mixture of the alcohol with red phosphorus, the vessel meanwhile being frequently shaken and well cooled. This operation is very tedious, and a

much better method is that devised by Walker.* The apparatus is shown in Fig. 57. 25 g. (30 c.c.) of alcohol are placed in the round flask (250–300 c.c. capacity) and 3 g. each of red and white phosphorus added, the latter being weighed under water in a small dish and then quickly dried with filter paper. 50 g. of iodine are placed in the funnel, the lower part of which is loosely plugged with glass wool. After attaching the condenser (reflux) the flask is heated in a water-bath. Alcohol vapour passes up the side tube, and the liquid returned from the condenser drops through the iodine, which is thus gradually introduced into the flask. Towards the end, the reaction tends to proceed more rapidly, since the iodide is more volatile, and is also a better solvent for iodine, than the alcohol; care is therefore necessary, especially with large quantities.

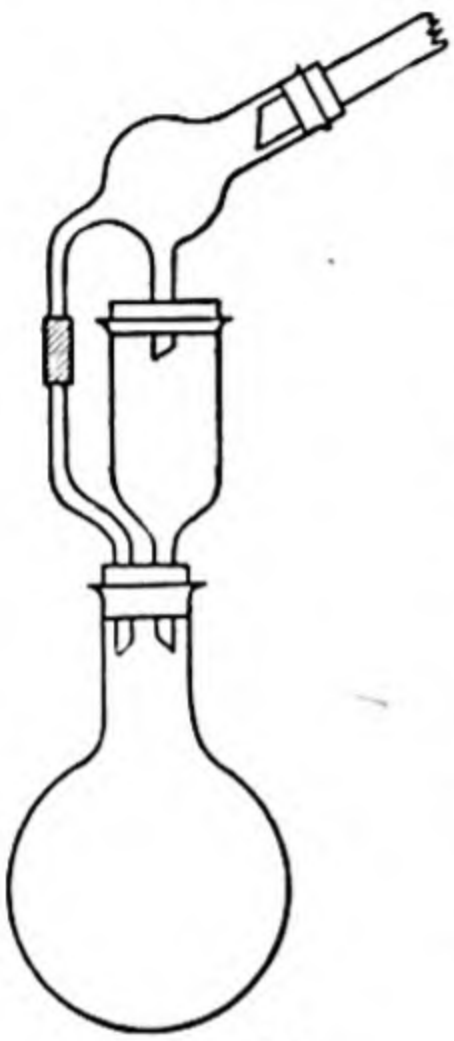


FIG. 57.

When the reaction is completed, pour a little water down the condenser, to destroy phosphonium compounds, detach the condenser, and distil from a water-bath. Wash the distillate with dilute sodium hydroxide until colourless, then with water, dry with calcium chloride, and distil from a small distilling flask. Yield 90 per cent. theory.

Ethyl iodide is a colourless, highly refractive liquid, of pleasant odour, insoluble in water, miscible with alcohol and ether; b.p. 72·5°; sp. gr. 1·975.

Methyl iodide, CH_3I, may be prepared in a similar manner. It is a colourless liquid of agreeable odour; b.p. 44°; sp. gr. 2·293.

The alkyl iodides are more readily decomposed than the corresponding bromides or chlorides, and soon acquire a brown colour owing to the separation of iodine. Walker claims that the keeping properties are much improved by the use of white phosphorus in the above method of preparation.

REACTIONS. The ease with which the alkyl iodides react

* Walker, *J.C.S.* (1892), 1971.

makes them available for the preparation of many classes of compounds, of which the following are examples :

Alcohols. Heat with aqueous alkali or moist silver oxide :

$$RI + KOH = R \,.\, OH + KI.$$
$$RI + AgOH = R \,.\, OH + AgI.$$

Ethers. Shake with dry silver oxide :

$$2RI + Ag_2O = R_2O + 2AgI.$$

Thioalcohols. Heat with alkali hydrosulphide solution :

$$RI + KSH = RSH + KI.$$

Thioethers. Heat with alkali sulphide solution :

$$2RI + K_2S = R_2S + 2KI.$$

Hydrocarbons. Allow to stand over sodium in dry ether :

$$2RI + 2Na = R \,.\, R + 2NaI.$$

Hydrocarbons (*unsaturated*). Boil with an alcoholic solution of alkali :

$$R \,.\, CH_2CH_2I + KOH = R \,.\, CH : CH_2 + KI + H_2O.$$

Cyanides. Distil with potassium (or silver) cyanide :

$$RI + AgCN = RCN + AgI.$$

Nitroparaffins. Distil with silver (or mercurous) nitrite :

$$RI + AgNO_2 = RNO_2 + AgI.$$

Primary iodides yield the nitro-compound as the chief product, with a little of the isomeric nitrite, R . O . NO. From secondary iodides the nitrite is the chief product, and from tertiary iodides it is the only product. The nitrites have much lower boiling points (V. Meyer, 1872).

Amines. Heat with ammonia in alcohol under pressure :

$$RI + NH_3 = R \,.\, NH_2 \,.\, HI.$$

Magnesium alkyl halides (*Grignard reagents*). Allow to stand over clean dry magnesium in dry ether :

$$RI + Mg = RMgI.$$

PARAFFINS (Alkanes), C_nH_{2n+2}

General methods of preparation :

(*a*) The action of heat on a mixture of the sodium salt of a fatty acid with an alkali :

$$CH_3COONa + NaOH = CH_4 + Na_2CO_3.$$

(*b*) Reduction of alkyl halides by means of nascent hydrogen :

$$C_2H_5Br + 2H = C_2H_6 + HBr.$$

(*c*) Hydrogenation of unsaturated hydrocarbons with the same number of carbon atoms :

$$CH_2 : CH_2 + 2H = CH_3CH_3.$$

(*d*) The action of sodium or zinc on alkyl halides :

$$2C_2H_5Br + 2Na = C_4H_{10} + 2NaBr.$$

(*e*) Electrolysis of solutions of the alkali salts of fatty acids :

$$2CH_3COONa + 2H_2O = C_2H_6 + 2CO_2 + 2NaOH + H_2.$$

193. Methane (Marsh gas), CH_4. Methane occurs in natural gas to the extent of 80–90 per cent. The gas, which is very abundant in the United States, is freed from the vapours of higher hydrocarbons and piped long distances for use in lighting and heating, either alone or mixed with water-gas. Such a mixture is very uniform in quality.

Mix together 10 g. of freshly-fused sodium acetate and 30 g. of granulated soda-lime, which has been previously heated and allowed to cool in the desiccator. Place the mixture in a hard glass test-tube or flask, heat carefully, and collect the gas over water. About 2 litres of gas will be evolved.

Show that bromine water and potassium permanganate are not affected by the gas, by adding these reagents respectively to two jars of the gas and shaking well. The gas is therefore saturated. With a third jar show that lime-water is not affected ; then burn the gas, noting the appearance of the flame, and show that carbon dioxide is produced.

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Another simple method for methane is the action of water on

aluminium carbide (Moissan, 1894). The reaction is aided by warming, or by addition of hydrochloric acid, but the gas contains hydrogen up to 20 per cent.

$$C_3Al_4 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$
$$C_3Al_4 + 12HCl = 3CH_4 + 4AlCl_3.$$

194. Ethane, C_2H_6. Ethane forms about 10 per cent. by volume of natural gas. It is prepared technically by the catalytic reduction of ethylene.

The second general method is convenient for small quantities.

In a 100 c.c. flask (Fig. 58), place a mixture of 20 g. of zinc dust and 2–3 g. powdered copper oxide. The calcium chloride tube is filled with coppered zinc, to remove vapour of ethyl bromide from the ethane: this is prepared by placing granulated zinc in dilute copper sulphate solution until it is coated with copper, then washing with water and finally with alcohol.

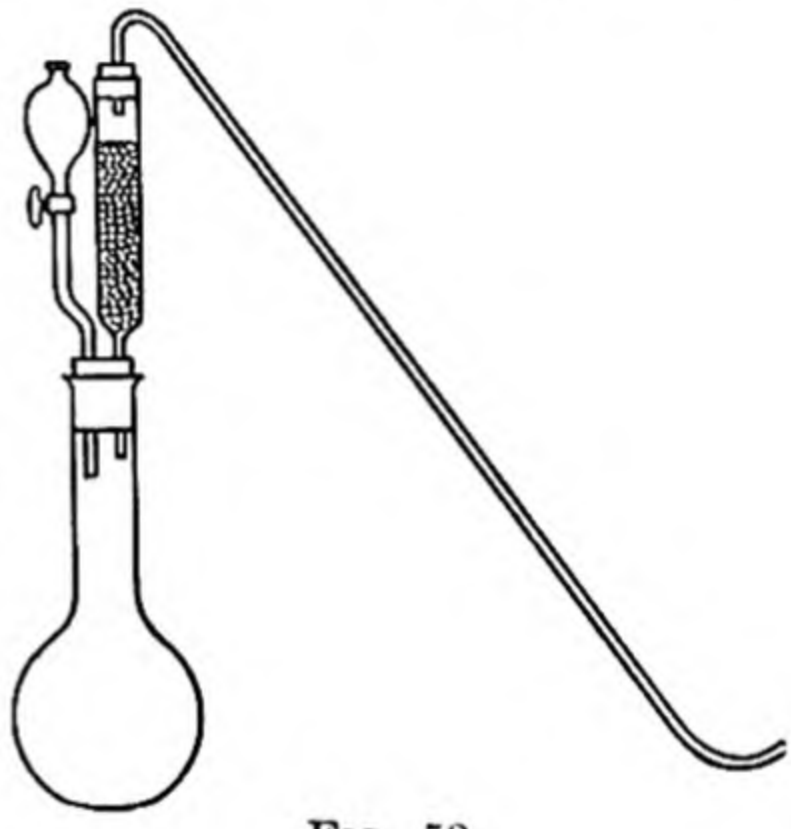


FIG. 58.

In the tap funnel place a mixture of 10 c.c. of ethyl bromide and 10 c.c. alcohol, and allow this to drop slowly on to the zinc copper couple in the flask. Ethane is evolved and is collected over water. Examine its properties as for methane.

By this method also methane may be prepared from methyl iodide,

$$CH_3I + CH_3OH + Zn = CH_4 + ZnI(OCH_3),$$

and ethylene from ethylene dibromide,

$$C_2H_4Br_2 + Zn = C_2H_4 + ZnBr_2.$$

THE ACTION OF SULPHURIC ACID ON ALCOHOLS

Although alcohols are not appreciably ionised, they react vigorously with sulphuric acid forming the alkyl hydrogen

sulphate and water. Much heat is developed. The reaction is reversible, and incomplete :

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5HSO_4 + H_2O.$$

The ethyl hydrogen sulphate so formed is decomposed again by water, reproducing the alcohol. It is also decomposed by excess of alcohol, forming the ether, and when heated alone, or with sulphuric acid, it yields the unsaturated hydrocarbon, ethylene.

It behaves as a monobasic acid, and may be isolated in the form of salts.

195. Potassium ethyl sulphate, $C_2H_5 . K . SO_4$. 60 c.c. of alcohol and 25 c.c. concentrated sulphuric acid are mixed carefully in a half-litre round flask. Much heat is liberated, and ethyl hydrogen sulphate is formed.

The reaction is incomplete unless a large excess of either alcohol or sulphuric acid be used. As the removal of much sulphuric acid from the product would be troublesome, excess of alcohol is employed, the above quantity being twice that theoretically required for 25 c.c. of acid. Heat the flask for 3 hours in a boiling water-bath under a reflux condenser. The mixture now contains much ethyl hydrogen sulphate and water, together with some free sulphuric acid and alcohol. Cool the flask under the tap, and pour the liquid into crushed ice or cold water in a large flask or dish. Neutralise with chalk or barium carbonate. This precipitates insoluble calcium or barium sulphate, while the calcium or barium ethyl sulphate is left in solution. Filter and evaporate to crystallising point. Colourless crystals of the salt

$$(C_2H_5 . SO_4)_2Ca . 2H_2O \quad \text{or} \quad (C_2H_5 . SO_4)_2Ba . 2H_2O$$

are obtained.

To prepare the potassium salt from these, dissolve in water and add carefully to this solution, or to the mother liquor, a dilute solution of potassium carbonate, until no further precipitate of calcium or barium carbonate is produced. On evaporating the filtered liquid colourless tables of the anhydrous potassium salt, $C_2H_5 . K . SO_4$, are obtained.

REACTIONS. 1. Heat a few crystals of the potassium salt in a dry test-tube. The salt melts and then decomposes, giving off ethylene gas, which can be ignited at the mouth of the test-tube, and leaving a residue of potassium bisulphate.

$$C_2H_5KSO_4 \rightarrow C_2H_4 + KHSO_4.$$

2. Dissolve a crystal of the potassium salt in water; add a little dilute hydrochloric acid and barium chloride. There is no precipitate. Boil for a few minutes. A white precipitate of barium sulphate is gradually formed, as ethyl sulphuric acid is hydrolysed by boiling water.

$$C_2H_5HSO_4 + H_2O \rightarrow C_2H_5OH + H_2SO_4.$$

OLEFINES (Alkenes), C_nH_{2n}

General methods of preparation:

(*a*) By the dehydration of alcohols:

$$C_2H_5OH(+H_2SO_4) = C_2H_4 + H_2O(+H_2SO_4).$$

(*b*) By the action of an alcoholic solution of caustic alkali on an alkyl halide:

$$C_2H_5I + KOH = C_2H_4 + KI + H_2O.$$

196. Ethylene (Ethene, Olefiant Gas), C_2H_4. The most convenient method is the action of sulphuric acid on alcohol. When a mixture of these substances in certain proportions is heated to about 140°, the sulphovinic acid first formed is decomposed with liberation of ethylene:

$$C_2H_5 . H . SO_4 \rightleftharpoons C_2H_4 + H_2SO_4.$$

The mixture, however, is liable to char, and it then evolves SO_2 and CO_2, which are troublesome.

Pure ethylene is most readily prepared by the action of syrupy phosphoric acid on alcohol, as described by Newth.*

Place 50–60 c.c. of the acid in a 200 c.c. distilling flask. Fit the flask with a cork carrying a thermometer and a dropping tube

* *J.C.S.* 1901, 915.

(Fig. 59), the end of the latter being drawn out to a fine point reaching to the bottom of the flask. The bulb of the thermometer must be in the liquid, and may be protected by being fitted with a capsule made of platinum foil. Boil the acid until the temperature rises to 200°, and then allow the alcohol to enter slowly. Keep the temperature between 200° and 220°. Pass the gas through a wash-bottle, standing in ice water, to condense the small quantities of ether and alcohol which are mixed with it.

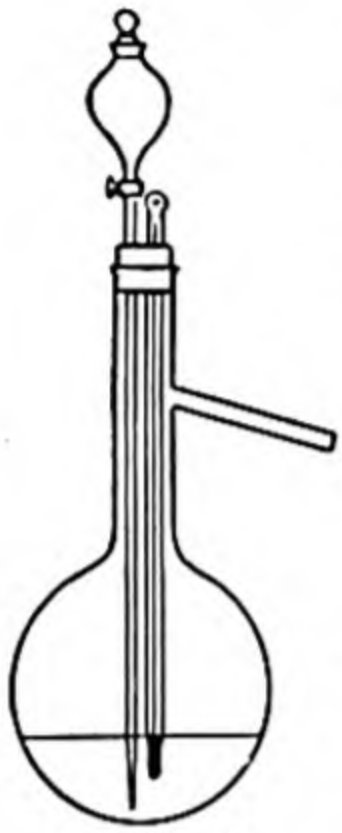


FIG. 59.

The action of the phosphoric acid is similar to that of sulphuric acid, phosphovinic acid being produced.

Better yields, up to 85 per cent., can be obtained by dehydrating the phosphoric acid at 250°, and keeping the temperature at this degree with addition of a little Cu, Fe or Al sulphate.

Collect several jars of the gas and show that it decolorises bromine and potassium permanganate; the gas is unsaturated. Show that it has no action on lime-water, but forms carbon dioxide when burned. A mixture with air is explosive.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

Ethylene is the chief constituent of the olefinic portion (50 per cent.) of the gas obtained by "cracking" heavy oils. It results from the application of the same process to natural gas, and gasoline, through such reactions as:

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \rightarrow \underset{\text{Ethylene}}{CH_2 : CH_2} + \underset{\text{Methane}}{CH_4}.$$

The products are condensed and the ethylene separated fractionally. It is used for many reactions, and also as a general anaesthetic in place of ether.

The characteristic reactions of the olefines are mainly due to the presence of the double bond, which tends to the formation of addition compounds.

197. Ethylene dibromide, $C_2H_4Br_2$. This may be prepared by absorbing ethylene gas in bromine. After collecting the gas

required in last experiment, allow the supply to pass into two glass wash-bottles, the first containing 20 c.c. (60 g.) and the second 10 c.c. of bromine, covered with water one inch deep. These wash-bottles should be kept cool in a trough of water. The bromine is gradually decolorised, forming a heavy colourless oil. Transfer this to a separating funnel, separate from the aqueous layer, and wash the oil with dil. alkali until all free bromine and hydrobromic and sulphurous acids are removed. The oil should now be colourless. Transfer it to a small Erlenmeyer flask, add some anhydrous sodium sulphate to dry it, cork the flask and allow to stand overnight. The oil may then be filtered into a small distilling flask and distilled. B.p. 131·5°, sp. gr. 2·17 at 20°.

Similar addition compounds are formed with chlorine, iodine and iodine monochloride. The dichloride, $CH_2Cl \cdot CH_2Cl$, is a colourless liquid of sp. gr. 1·26, boiling at 83·5°. It is much used as a solvent. Hypochlorous acid in aqueous solution unites with ethylene to form the chlorohydrin (2-chloroethanol),

$$CH_2 : CH_2 + HO \cdot Cl \rightarrow CH_2Cl \cdot CH_2OH,$$

and similar results are obtained with dilute chlorine water or bromine water.*

Oxidation with dilute permanganate solution (Baeyer's test for olefines) yields the glycol :

$$CH_2 : CH_2 + O + H_2O \rightarrow CH_2OH \cdot CH_2OH,$$

while atmospheric oxygen gives a good yield of formaldehyde † :

$$CH_2 : CH_2 + O_2 \rightarrow 2CH_2O.$$

Catalytic hydrogenation in presence of finely divided nickel (Sabatier, 1907) takes place readily at 150°, or in presence of finely divided platinum (Willstätter, 1908) at the ordinary temperature :

$$CH_2 : CH_2 + H_2 \rightarrow CH_3 \cdot CH_3.$$

Some of these reactions are of great technical importance.

* Read, *J.C.S.* 1920, 1214 ; 1928, 745.

† Willstätter, *Z. ang. Ch.* 1919, 82, 330.

ACETYLENES (Alkynes), C_nH_{2n-2}

198. A general method of preparation is to boil an alkene dihalide with alcoholic alkali :

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

Acetylene (Ethyne), C_2H_2. In a small flask place half a stick of caustic potash and 10 c.c. alcohol and shake gently until the potash dissolves. Then add 2–3 c.c. ethylene dibromide and warm gently, collecting the evolved acetylene over water. Examine its behaviour with permanganate and bromine water, and on burning.

Acetylene is manufactured from calcium carbide by the action of water :

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

Place some pieces of carbide in a small distilling flask fitted with a tap funnel. From the latter allow water to drop slowly on to the carbide, when acetylene will be rapidly and continuously evolved. The gas may be collected over water, and its properties examined as above.

REACTIONS. 1. Acetylene unites with bromine to form a dibromide and a tetrabromide : the latter is a colourless liquid of sp. gr. 2·96, and b.p. 114° at 12 mm. It is prepared similarly to ethylene dibromide.

2. When the gas is passed into an ammoniacal solution of cuprous chloride, a dark red-brown precipitate of cuprous acetylide is formed :

$$Cu_2Cl_2 + C_2H_2 + 2NH_3 = C_2Cu_2 + 2NH_4Cl.$$

The precipitate is stable in water, but very explosive when dry. It is decomposed by hydrochloric acid, liberating pure acetylene :

$$C_2Cu_2 + 2HCl = C_2H_2 + Cu_2Cl_2.$$

An acetone solution of acetylene serves as a useful reagent for cuprous salts.

Ammoniacal silver solutions similarly give a white precipitate of silver acetylide, Ag_2C_2.

Acetylene is of great industrial importance, and from it are manufactured acetaldehyde, alcohol, acetic acid, *n*-butyl alcohol,

acetone, vinyl acetate and chloride and their plastic polymers; tetrachloroethane, trichloroethylene, and other important solvents. Polymerised chlorinated derivatives are used as rubber substitutes, such as duprene (chloroprene rubber).*

ETHERS (Alkoxyalkanes), $C_nH_{2n+1}OC_mH_{2m+1}$

General methods of preparation :

(*a*) By the action of an alkyl halide on an alkoxide :

$$RI + NaOR_1 = ROR_1 + NaI.$$

(*b*) By the dehydration of alcohols, usually by means of sulphuric acid ; the alkyl hydrogen sulphate is first formed, and reacts with a second molecule of the alcohol, producing the ether :

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

$$C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$

The ether and some of the water distil, while sulphuric acid is regenerated. A large quantity of ether may therefore be prepared from a relatively small amount of sulphuric acid.

Bruce & Harper

199. Ethyl ether (Ethoxyethane), $(C_2H_5)_2O$. In a half-litre distilling flask, connected to a long condenser (see preparation of aldehyde, par. 200), and fitted with a thermometer reaching nearly to the bottom, and a tap funnel, place a mixture of 120 c.c. alcohol and 80 c.c. concentrated sulphuric acid. Heat the flask on a sand-bath to 140°, and keeping the temperature at 140–145°, run in alcohol as fast as the ether distils. This should be collected in a well-cooled receiver, connected to the condenser by means of an adapter. It is advisable also to place a tinplate or cardboard screen across the working bench between the receiver and the burner, as ether vapour is very inflammable.

Collect about half a litre of ether, transfer to a separating funnel and wash with dilute sodium hydroxide to remove sulphurous acid. Then wash with a strong solution of calcium chloride or common salt to remove alcohol, and finally transfer

* W. H. Carothers and others, *J. Amer. C.S.* **53**, 4203 (1931).

the ether to a dry flask and allow to stand over dry calcium chloride. The last traces of water and alcohol can only be removed with metallic sodium, which has no action on pure ether.

Ether is a colourless, mobile liquid, boiling at 35°, and of sp. gr. ·720 at 15°. It burns with a luminous flame, is miscible with alcohol, but only sparingly soluble in water (9 vols.).

It is decomposed on heating with hydrogen iodide :

$$R . O . R + HI = R . OH + RI.$$

$$R . O . R + 2HI = H_2O + 2RI.$$

Note. In all operations with ether, the neighbourhood of flames must be avoided.

Dry ether. In spite of the efficiency of modern methods of distillation, commercial ethers contain some water and alcohol. These must be removed when the ether is required for use with sodium or other materials that react with hydroxylic compounds.

To prepare dry ether, place a sufficient quantity, say 500 c.c., in a flask or bottle closed with a cork bearing an open calcium chloride tube, add granular calcium chloride to fill half the bulk of the liquid, and allow to stand for at least 24 hours. Decant the liquid into another bottle similarly furnished with a $CaCl_2$ tube, and add a quantity of sodium wire so that it is evenly distributed in and completely covered by the ether. Hydrogen is slowly evolved so long as any traces of alcohol or water remain. The sodium hydroxide and ethoxide formed are insoluble in ether and fall as a sediment. Several days may be necessary for complete drying. The ether should be kept in this bottle and decanted for use as required.

OXIDATION OF ALCOHOLS

Alcohols may be oxidised by the moderate action of oxidising agents, producing first the aldehyde and then, by further oxidation, the corresponding acid.

$$C_2H_5OH + O = CH_3CHO + H_2O,$$

$$CH_3CHO + O = CH_3 . COOH.$$

Catalytic processes are now much used.

ALDEHYDES (Alkanals), $C_nH_{2n+1}CHO$

200. Acetaldehyde (Ethanal), $CH_3 . CHO$, is manufactured by passing an air-alcohol mixture over a silver catalyst, kept at a dull red heat by the partial combustion of the alcohol. Some is obtained from the first runnings of the alcohol stills. An important source is acetylene, which, when passed into a well-agitated suspension of Hg_2SO_4 in 10–40 per cent. H_2SO_4 at 40°–80° C., forms a mercuric compound which decomposes into acetaldehyde. This passes off in the gas and is scrubbed and rectified :

$$CH \vdots CH + H_2O \rightarrow CH_3CHO.$$

For laboratory experiments, dichromate is usually employed to oxidise the alcohol.

In a flask of 1·5–2 l. capacity (Fig. 60) place 140 g. coarsely powdered potassium dichromate and 550 c.c. water. The flask

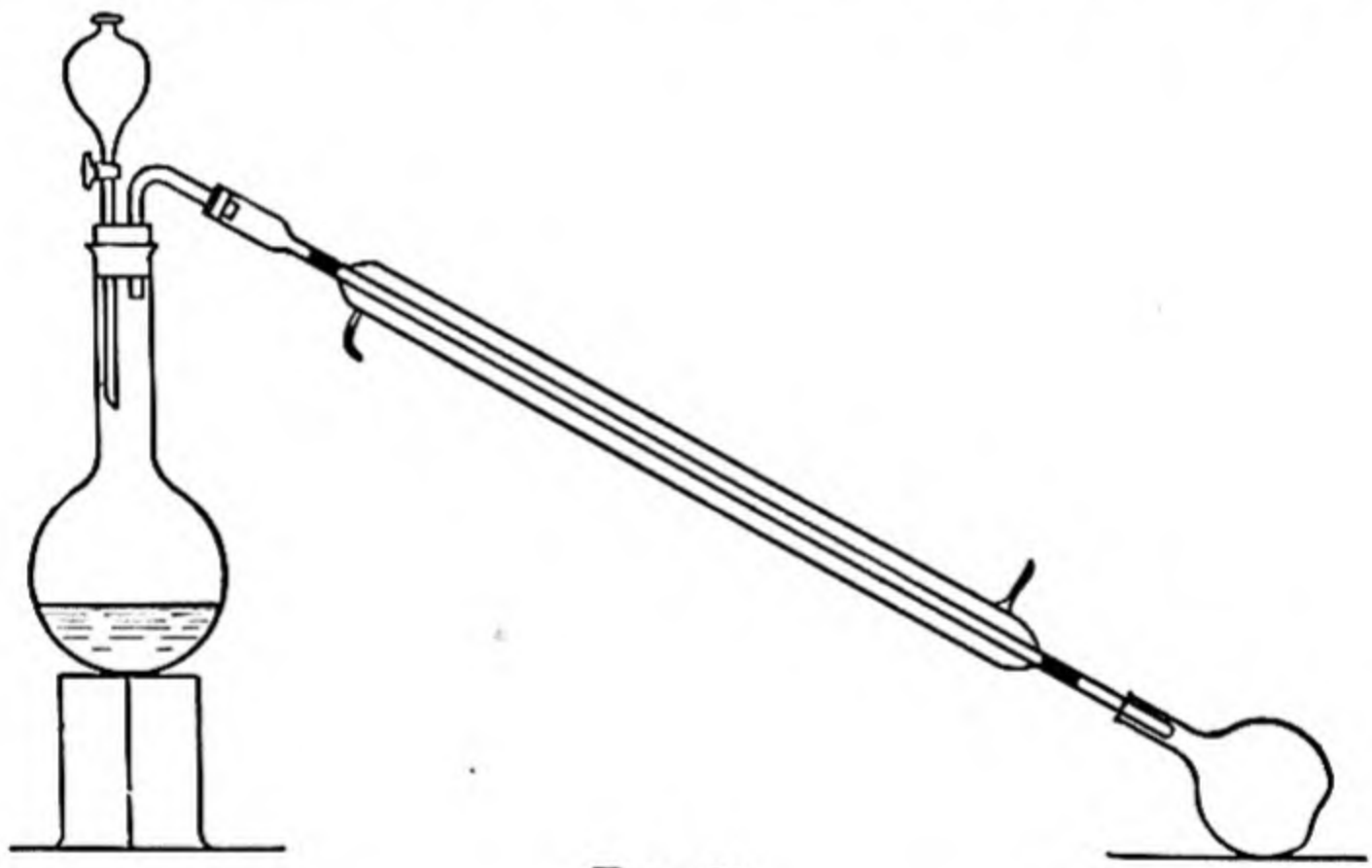


Fig. 60.

is placed on a sand-bath, and is fitted with a tap funnel and connected with a good condenser and a receiver cooled in ice water. From the funnel introduce a cooled mixture of 148 g. (190 c.c.) alcohol and 184 g. (100 c.c.) conc. sulphuric acid. The dichromate is reduced, as shown by the darkening of colour, and sufficient heat is evolved to cause the aldehyde to distil. When the first reaction subsides, heat the liquid and continue the distillation

until all aldehyde has passed over ; no smell of aldehyde should then be detected on opening the flask, and the distillate should occupy 180–190 c.c. The residue in the flask may be used to obtain chrome alum.

This distillate is a mixture of aldehyde, alcohol and water, and may be tested for aldehyde as follows :

REACTIONS. 1. Warm with ammoniacal silver solution in a test-tube placed in a beaker of hot water. A mirror of metallic silver is produced. Fehling's solution also is reduced.

$$C_2H_4O + Ag_2O = 2Ag + C_2H_4O_2 \text{ (acetic acid).}$$

2. Apply the iodoform test (189, 5). A yellow precipitate of iodoform is produced.

3. Add a few drops to a small quantity of a saturated solution of sodium bisulphite and shake well. A white, crystalline addition compound, $CH_3CHOH \,.\, SO_3Na$, separates on standing.

4. A solution of magenta (rosaniline hydrochloride) which has been just decolorised with sulphur dioxide (Schiff's reagent) has the intense red-violet colour restored by a few drops of aldehyde.

201. Aldehyde ammonia. The aldehyde obtained above may be purified by conversion into aldehyde ammonia.

$$CH_3CHO + NH_3 = CH_3 \,.\, CH\begin{<}OH\\NH_2\end{>}.$$

To the flask containing the impure aldehyde connect, by means of an adapter or by inclining the flask, a reflux condenser (Fig. 61), the upper end of which is connected by a glass tube with a 100 c.c. pipette, which passes nearly to the bottom of the first of two small wash-bottles connected in series. These last contain each about 25 c.c. of ether, and are kept cool by standing in ice water. Through the condenser a stream of water at 30–40° flows. Place a few pieces of broken pot in the flask, and boil the liquid gently until all aldehyde has passed over into the ether. The water and alcohol are condensed and returned to the flask.

Now saturate this ethereal solution of aldehyde with ammonia, by passing the dry gas through the pipette, still keeping

the wash-bottles in ice water. After a short time colourless crystals of aldehyde ammonia separate. These may be filtered at the pump, washed with a little ether and dried.

To obtain pure aldehyde from this substance, place it in a small flask, cover with a cold mixture of equal volumes of sulphuric acid and water, and distil from a water-bath, collecting the aldehyde in a well-cooled receiver. The distillate may be dehydrated over calcium chloride, and again distilled from this.

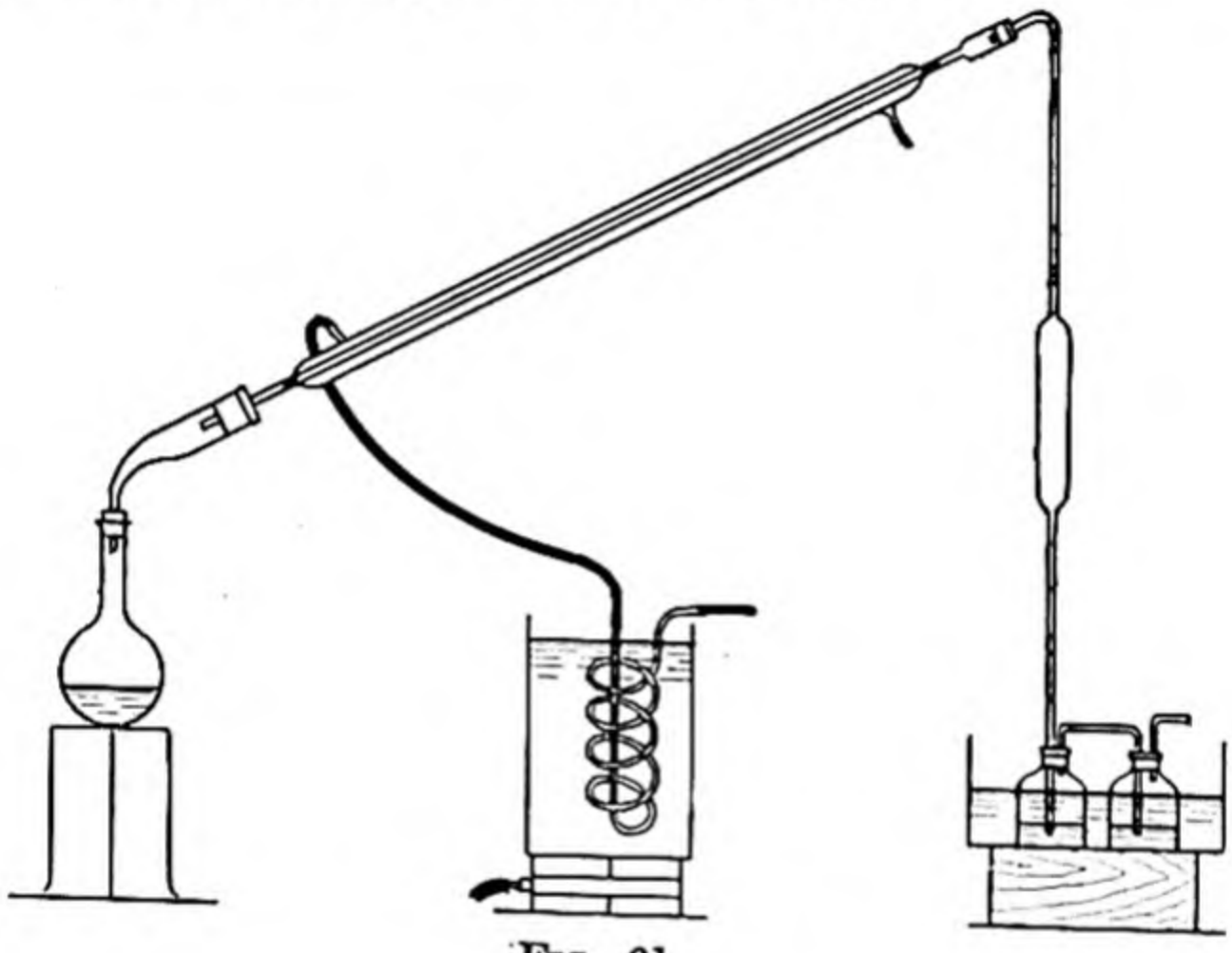


FIG. 61.

Pure aldehyde is a colourless liquid, with a pleasant smell. B.p. 21° ; sp. gr. ·807 at 0°. It mixes with water, alcohol and ether in all proportions.

202. Formaldehyde (Methanal), H . CHO. Formaldehyde bears the same relation to methyl alcohol that acetaldehyde bears to ethyl alcohol. It is a gas with a characteristic smell and antiseptic properties, condensing to a liquid at −21°, and is known chiefly in the form of its aqueous solution, formalin, which contains about 40 per cent. of the gas.

Formaldehyde may be prepared by the general methods for preparing aldehydes, and is readily obtained by the oxidation of methyl alcohol with atmospheric oxygen.

In a small beaker place a few c.c. of methyl alcohol. Warm the alcohol and hold in the vapour a hot spiral of platinum wire. Observe the effect of holding the spiral at different distances from the surface of the liquid, and note the peculiar smell of formaldehyde.

Owing to its antiseptic properties many kinds of formaldehyde lamp have been introduced, and a simple one may be made as follows: Fill an ordinary spirit lamp with methyl alcohol and arrange round the wick a spiral of platinum wire, light the lamp for a short time and then extinguish the flame. A spiral of the proper size will continue to glow, and a constant production of formaldehyde will result.

On a large scale formaldehyde is produced by aspirating air through heated methyl alcohol and passing the mixture through an "oxidiser" containing copper or silver gauze at 300° as a catalyst. The product is dissolved in water to make a 40 per cent. solution known commercially as formalin, having a sp. gr. of 1·08. The solution when evaporated leaves paraformaldehyde, $(HCH : O)_n$, as a colourless solid.

Formaldehyde is also obtained by catalytic union of carbon monoxide and hydrogen, by modifying the conditions of the Patart process:

$$CO + H_2 \rightarrow CH_2O,$$

and by Willstätter's method of catalytic oxidation of ethylene:

$$CH_2 : CH_2 + O_2 \rightarrow 2CH_2O.$$

REACTIONS. 1. Warm a few c.c. of formalin with ammoniacal silver solution in a test-tube placed in hot water. A mirror of metallic silver is produced. Fehling's solution also is reduced.

2. Ammonium chloride solution causes the formation of crystalline hexamethylenetetramine (urotropine), $(CH_2)_6N_4$, which separates on evaporation:

$$6CH_2O + 4NH_4Cl = (CH_2)_6N_4 + 6H_2O + 4HCl.$$

Titration of the free acid gives a means of estimating formaldehyde (427).

3. Formaldehyde gives Schiff's test for aldehydes (200, 4).

4. Add a drop of formalin to 100 c.c. of water. Then add 2 c.c. of a 1 per cent. solution of phenylhydrazine hydrochloride, 1 c.c. of a 5 per cent. solution of potassium ferricyanide and a few c.c. of conc. hydrochloric acid. A rose-red colour is produced (Schryver's test). This reaction will detect 1 part of formaldehyde in 100,000 parts of water.

203. Acetic acid (Ethanoic acid), $CH_3 . CO . OH$. Acetic acid is manufactured in several ways. The oldest method is the acetic fermentation of dilute alcoholic liquors (6–10 per cent.) in which the alcohol is oxidised by air through the intermediary of the ferment, *bacterium aceti*. The concentration of the acid produced in this way does not exceed 11–12 per cent.

The destructive distillation of wood in iron retorts at temperatures rising to 450–500° yields an aqueous distillate called pyroligneous acid. This contains about 5 per cent. of acetic acid, with a little methyl alcohol and acetone. It is either neutralised with lime, and the volatile liquids distilled, leaving "grey acetate of lime," or the whole liquid is fractionated by a continuous distillation method (49).

Modern methods are based on the catalytic oxidation of acetaldehyde by air. This may be done by blowing air through a suspension of a manganese catalyst in acetaldehyde containing some acetic acid :

$$2CH_3CHO + O_2 = 2CH_3COOH ;$$

the acid content is thus increased to about 97 per cent. The excess aldehyde is scrubbed out and returned in the air current to the acetic acid vessels.

In a half-litre round flask connected with an upright condenser place 30 g. coarsely powdered potassium dichromate and a cold mixture of 30 g. conc. sulphuric acid and 20 c.c. water. From the top of the condenser introduce slowly a mixture of 10 c.c. alcohol and 10 c.c. water, so that the reaction does not become too violent. When all is introduced, boil gently on a sand-bath until the smell of aldehyde is no longer observed on opening the flask. This will require about half an hour. The alcohol is now completely oxidised to acetic acid.

Now rearrange the condenser, and distil until the distillate is only slightly acid. The pure acid is best obtained from its salts. Neutralise the dilute acetic acid with sodium carbonate, filter and crystallise the salt. Sodium acetate forms colourless crystals, containing three molecules of water, $CH_3 . COONa . 3H_2O$.

To obtain pure acetic acid, the sodium salt may be mixed with conc. sulphuric acid and distilled. The acid is a colourless liquid, solidifying readily on cooling; m.p. 17°; b.p. 118°; sp. gr. 1·055 at 15°. The acid has a pungent smell, and blisters the skin. The salts are soluble in water, and are decomposed on heating, giving off inflammable vapours (acetone, marsh gas, etc.) and leaving a residue of the metal or its carbonate or oxide.

$$(CH_3COO)_2Ca = CaCO_3 + CH_3 . CO . CH_3 \text{ (acetone)}.$$

Reactions. 1. Mix a little sodium acetate in a watch glass with a few drops of conc. sulphuric acid, and note the smell of acetic acid.

2. To a little dry sodium acetate or glacial acetic acid in a test-tube add a little alcohol and conc. sulphuric acid, and warm gently. Ethyl acetate is formed, and is indicated by its pleasant fruity smell (compare 189, 3).

3. To a neutral solution of an acetate add ferric chloride solution. A red-brown colour, due to ferric acetate, is produced, and on boiling, basic ferric acetate is precipitated.

$$(CH_3COO)_3Fe + 2H_2O = (CH_3COO)Fe(OH)_2 + 2CH_3COOH.$$

4. In concentrated solutions silver nitrate gives a white precipitate of silver acetate, soluble in hot water without reduction (compare formates, 205, 2).

204. Acetates. The salts of acetic acid are readily obtained by neutralising the dilute acid with the oxide or the carbonate of a metal.

Sodium acetate, $CH_3COONa . 3H_2O$, has been described above. It is very soluble in water and is used for artificial cooling. The water of crystallisation is expelled about 200°, and the anhydrous salt is a valuable desiccating agent.

Ammonium acetate, CH_3COONH_4, forms deliquescent crystals, and is obtained by saturating the acid with ammonia. The solution on evaporating loses ammonia, and the solid when heated melts and loses water with formation of acetamide (212) :

$$CH_3COONH_4 - H_2O = CH_3CONH_2.$$

Lead acetate (Sugar of Lead). Dilute 50 c.c. of glacial acetic acid with 100 c.c. of water and neutralise with litharge or lead carbonate, warming meanwhile on the water-bath. Filter and evaporate the solution of lead acetate. Colourless crystals are obtained, having the composition $(CH_3COO)_2Pb \cdot 3H_2O$.

Basic lead acetate, $Pb(OH)C_2H_3O_2$, is obtained by boiling a solution of lead acetate with litharge (169). These salts are used for the preparation of **white lead** and other compounds.

Copper acetate, $(CH_3COO)_2Cu \cdot H_2O$. To a solution of copper sulphate, made by dissolving 20 g. of the salt in water, add sodium carbonate to precipitate the copper as basic carbonate. Filter by suction, wash well, transfer to a porcelain dish, and warm with acetic acid till dissolved. The acid should be diluted before use, and added in slight excess. Evaporate till concentrated and allow to crystallise.

$$CuCO_3 + 2CH_3COOH = (CH_3COO)_2Cu + H_2O + CO_2.$$
$$Cu(OH)_2 + 2CH_3COOH = (CH_3COO)_2Cu + 2H_2O.$$

Copper acetate is used as a mordant, chiefly in the form of verdigris, a basic copper acetate approximately of the formula $2Cu(C_2H_3O_2)_2 \cdot CuO$, but of varying composition. This is also used as a green pigment, but is not good, the colour being altered by moisture and light.

Acetates of aluminium, chromium and iron are used as mordants in dyeing and printing.

205. Formic acid (Methanoic acid), $H \cdot COOH$, may be obtained by oxidising methyl alcohol, but is most conveniently prepared from oxalic acid, by decomposing it in presence of glycerol, which prevents the further decomposition of the formic acid.

$$H_2C_2O_4 = H \cdot COOH + CO_2.$$

In a large retort place 100 c.c. glycerol and 50 g. crystallised oxalic acid. Attach a condenser, and fit a thermometer in the retort, with the bulb dipping into the liquid. Heat on a sand-bath. At 90° carbon dioxide begins to be evolved, and at 100–110° water and formic acid distil. When the temperature reaches 110° allow to cool to about 80°, add another 50 g. of oxalic acid and distil as before to 110°. Repeat until 150–200 g. oxalic acid have been used. The residue in the retort still contains some glyceryl formate. It should be transferred to a large flask, and distilled with steam until the distillate is no longer acid. The distillate consists of an aqueous solution of formic acid. It may be converted into

Lead formate, $Pb(HCO.O)_2$. Neutralise the heated liquid by stirring in lead carbonate until the addition of more produces no further effervescence. Filter, wash the residue, and evaporate the filtrate. The lead formate crystallises in long colourless needles.

Pure formic acid may be obtained by heating the dry lead salt to 100° in a stream of dry sulphuretted hydrogen,

$$Pb(HCOO)_2 + H_2S = PbS + 2H.COOH,$$

or by distilling the dilute acid until the constant boiling hydrate ($4CH_2O_2 + 3H_2O$) is obtained, boiling at 107·1° at 760 mm. This contains 77 per cent. of formic acid. Dissolve in this, anhydrous oxalic acid, which on crystallising will remove the water. The liquid remaining is now almost pure formic acid, and may be distilled again.

Formic acid is now manufactured from carbon monoxide by absorption in concentrated sodium hydroxide solution at 150–200° and 10–20 atmospheres pressure :

$$CO + HONa = H.COONa.$$

Similar reactions with sodium alkoxides yield sodium salts of the higher acids :

$$CO + \underset{\text{Sodium methoxide}}{CH_3ONa} = \underset{\text{Sodium acetate}}{CH_3COONa}.$$

$$CO + \underset{\text{Sodium ethoxide}}{C_2H_5ONa} = \underset{\text{Sodium propionate}}{C_2H_5COONa}.$$

Properties. A colourless, mobile liquid, f.p. 8·6°, b.p. 100·6°, sp. gr. 1·22 at 20°. It mixes with water and alcohols in all proportions, has a pungent, acid smell, and raises blisters on the skin.

REACTIONS. 1. Heated with conc. sulphuric acid, formic acid and formates decompose into carbon monoxide and water.

$$H . COOH = H_2O + CO.$$

2. Formic acid reduces ammoniacal silver solutions forming a mirror of metallic silver, and mercuric chloride solution giving a white precipitate of mercurous chloride.

3. Neutral solutions of formates give a red-brown colour with ferric chloride, and on boiling, a brown precipitate of basic ferric formate (compare acetic acid, 202, 3).

4. Ethyl formate, recognised by its odour, is produced when formic acid or a formate is added to a mixture of 1 c.c. sulphuric acid with 2 c.c. of alcohol, and warmed.

ETHEREAL SALTS (Esters)

The process of esterification is discussed in par. 68, and reference should be made to this.

206. Ethyl acetate, $CH_3 . CO . OC_2H_5$. In a half-litre distilling flask place a mixture of 50 c.c. alcohol and 50 c.c. conc. sulphuric acid. Fit the flask with a tap-funnel and a thermometer, the latter dipping into the liquid, and with a condenser and receiver. The flask is heated on a sand-bath until the thermometer indicates 140°, and at this temperature a mixture of 100 c.c. alcohol and 100 c.c. glacial acetic acid is dropped into the liquid, as rapidly as ethyl acetate distils over. The distillate is a mixture of ethyl acetate, alcohol, water and acetic acid, with sulphurous acid if any charring has occurred. It is washed with sodium carbonate solution in a separating funnel until neutral, then with saturated calcium chloride solution to remove alcohol, and then dried over anhydrous sodium sulphate.

Filter into a dry distilling flask, and distil over a naked flame; some ether passes over first. Collect as ethyl acetate the portion from 74–80°.

Ethyl acetate is a colourless liquid, with a pleasant fruity odour. It mixes with alcohol and ether in all proportions and is soluble in about 11 times its volume of water. B.p. 77° ; sp. gr. ·9072 at 15°.

Amyl acetate, $CH_3 . CO . OC_5H_{11}$. Commercial amyl compounds are generally prepared from fusel oil, the residue left in the rectification of alcohol. This consists chiefly of inactive amyl alcohol, with some active amyl alcohol, $C_2H_5 . CH(CH_3) . CH_2OH$, various esters, etc., and compounds prepared from it are not pure.

Mix carefully in a round-bottomed flask 25 c.c. of commercially pure amyl alcohol, 25 c.c. glacial acetic acid, and 12·5 c.c. conc. sulphuric acid. Heat on a water-bath under a reflux condenser for five hours, and allow to stand overnight. When cold, pour the mixture into cold water, and allow to settle in a separating funnel. The upper layer is the ester. Wash with a concentrated solution of sodium carbonate, then with water, dry over sodium sulphate and distil.

iso-Amyl acetate is a colourless liquid, sparingly soluble in water, miscible with organic solvents. B.p. 140° ; $D\frac{15}{4} = ·875$.

It smells of jargonelle pears, and is used in flavouring, and as a solvent for camphor, resins and cellulose esters.

***n*-Butyl acetate,** boiling at 126°, may be prepared in the same way. It is largely used as a solvent and for lacquers.

Ethyl nitrite, $C_2H_5O . NO$. Dissolve 34·5 g. of sodium nitrite in 120 c.c. of water contained in a half-litre flask.

Add 7·5 c.c. of concentrated sulphuric acid to a mixture of 40 c.c. of alcohol with 75 c.c. of water. Cool this mixture with ice, and while stirring continually, pour into it slowly the solution of sodium nitrite. The ethyl nitrite separates as an upper layer. Run off the lower aqueous layer from a separating funnel, wash the nitrite with very cold water, and dry with calcium chloride in a corked flask. Distil from a small dry distilling flask.

Ethyl nitrite is a colourless liquid with a smell recalling that of apples. It is slightly soluble in water and miscible with alcohol. B.p. 18° ; sp. gr. ·900 at 15·5°. It is neutral in reaction, but on keeping it becomes acid, and evolves nitric oxide. The acidity is

due to acetic acid produced by atmospheric oxidation of acetaldehyde, which is always present in the preparation.

Ethyl nitrite (spirit of nitrous ether) is used as a diaphoretic and diuretic.

207. Aldol condensation. This reaction of aldehyde (200) is carried out on a manufacturing scale (British Industrial Solvents Ltd.) by boiling with NaOH solution in a copper agitator fitted with reflux condenser. Subsequent distillation yields the unsaturated crotonaldehyde, b.p. 103°, with an azeotropic mixture (47, 49) boiling at 85°, and from this on hydrogenation with gas from the acetone plant (217),

$$2CH_3CHO \xrightarrow{NaOH} \underset{\text{Aldol}}{CH_3CH(OH)CH_2CHO} \xrightarrow{-H_2O}$$

$$\underset{\text{Crotonaldehyde}}{CH_3CH:CHCHO} \xrightarrow[H_2]{} \underset{n\text{-Butaldehyde}}{CH_3CH_2CH_2CHO} \xrightarrow[H_2]{} \underset{n\text{-Butanol}}{CH_3CH_2CH_2CH_2OH}$$

using a copper catalyst, butaldehyde and butyl alcohol are obtained. The last is a very important solvent.

208. Chloral hydrate, $CCl_3 . CH(OH)_2$. This is prepared by the action of chlorine on alcohol, which is thus oxidised and chlorinated in the same process. Chloral itself, or trichloroacetaldehyde, is a liquid of sp. gr. 1·512 (20°), boiling at 97°. It polymerises on standing to metachloral, and combines readily with water to form the solid crystalline hydrate, melting at 57°.

It is soluble in water, alcohol, etc., and gives the reactions of aldehydes, reducing Fehling's solution and ammoniacal silver nitrate. Schiff's reaction is given by chloral, but not by chloral hydrate.

In contact with sulphuric acid, chloral hydrate loses water forming chloral, which may be distilled.

With aqueous sodium hydroxide it decomposes with formation of chloroform :

$$CCl_3 . CHO + NaOH = CHCl_3 + H . COONa.$$

209. Chloroform, $CHCl_3$. 150 g. of good bleaching powder are triturated in a large mortar with 500–600 c.c. water, using the

water in portions, and the milky liquid is poured into a 2-litre flask. To this liquor add 35 c.c. alcohol or acetone, connect with a good condenser, and warm gently on a sand-bath. Chloroform and water, with a little alcohol or acetone, distil. When no more can be obtained, dilute the distillate with water to precipitate the chloroform completely, separate in a funnel, wash with caustic soda, then with water, and dry in a corked flask with dry calcium chloride. Distil the chloroform from a small dry distilling flask.

Chloroform is a colourless, highly refractive liquid of sp. gr. 1·526 at 0° ; b.p. 61° ; miscible with alcohol or ether, but only slightly soluble in water. It has a sweet smell, and is a valuable anaesthetic. For this purpose it must be quite pure. In presence of air and light it decomposes slowly with formation of hydrochloric acid and carbonyl chloride :

$$CHCl_3 + O = HCl + COCl_2.$$

To counteract this, pure chloroform is mixed with about one per cent. of alcohol, and kept in dark bottles filled to the stopper.

Reactions. 1. To test the purity, 2 c.c. are shaken with an equal volume of water. The water should show no acidity, nor any cloudiness with silver nitrate solution.

2. A few drops heated with a drop of aniline and a little alcoholic potash yield phenyl isonitrile, of unpleasant, nauseating odour :

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5NC + 3KCl + 3H_2O.$$

Bromoform, $CHBr_3$, can be prepared from acetone or alcohol by the action of bromine and potash, the mixture being kept cool at first, then refluxed for an hour and steam distilled. Bromoform is a colourless liquid, b.p. 151°, sp. gr. 2·9, practically insoluble in water.

Iodoform, CHI_3. In a quarter-litre flask place 20 g. crystallised sodium carbonate and 100 c.c. water and warm on the steam or water-bath. When the carbonate is dissolved, add 10 c.c. acetone, and then, keeping the temperature at 60–70°, add gradually 10 g. of powdered iodine. Iodoform separates as a pale yellow crystalline powder. Filter on the pump, wash with cold water, and crystallise from a little acetone.

Iodoform crystallises in thin, yellow, hexagonal plates, melting at 119°. Insoluble in water; soluble in alcohol, ether, chloroform, etc. It is volatile on heating and the vapour has anaesthetic properties. (Note the structural resemblance to chloroform.) It was formerly much used in surgery as an antiseptic dressing, and in ointments, and has a peculiar and very persistent odour.

210. Carbon tetrachloride, CCl_4, a very important solvent, is made by the action of chlorine on hot chloroform, or on carbon bisulphide in presence of aluminium chloride or manganese chloride:

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2,$$

the sulphur chloride is separated by distillation, or boiled with more bisulphide:

$$CS_2 + 2S_2Cl_2 = CCl_4 + 6S.$$

Carbon tetrachloride is a colourless liquid boiling at 77°, sp. gr. 1·631 at 0°. It is insoluble in water, and therefore useful for extractions from aqueous solutions. It is incombustible, and used as a fire extinguisher under the name of *pyrene*.

211. Acetyl chloride, $CH_3 . COCl$. A convenient method for the preparation of acid chlorides is that in which the pure acid is mixed with phosphorus trichloride:

$$3CH_3 . CO . OH + 2PCl_3 = 3CH_3 . CO . Cl + P_2O_3 + 3HCl.$$

An apparatus similar to that used for ethyl bromide (191) may be employed, except that the receiver should be protected from moisture by means of a calcium chloride tube (Fig. 62).

FIG. 62.

100 g. of glacial acetic acid are placed in the flask, which stands in a bath of cold water, and 80 g. PCl_3 are added from the tap-funnel. The mixture is heated gently until the evolution of HCl has ceased, and the liquid, which has now separated into two layers, is distilled by raising

the temperature of the water-bath to boiling point. The upper layer, consisting of CH_3COCl, passes over, leaving phosphorous acid behind. The liquid should be redistilled, using a thermometer, the receiver being kept dry as before.

Acetyl chloride is a colourless mobile fuming liquid, b.p. 55°, sp. gr. 1·130. It is readily decomposed by water forming acetic and hydrochloric acids :

$$CH_3CO\,.\,Cl + H_2O = CH_3CO\,.\,OH + HCl,$$

and reacts with alcohols to form ethereal salts.

212. Acetamide, $CH_3CO\,.\,NH_2$. The chlorine atom in acid chlorides is readily replaced by $-NH_2$, by the action of ammonia. Mix a few drops of acetyl chloride with a little dry ether in a test-tube, and add a few drops of conc. ammonium hydroxide. A white precipitate is at once obtained :

$$CH_3\,.\,CO\,.\,Cl + 2NH_3 = CH_3\,.\,CO\,.\,NH_2 + NH_4Cl.$$

This method is often convenient, but if a quantity is to be prepared, dry ammonia gas should be used, and the amide may be extracted from the drained precipitate by means of chloroform or another suitable solvent, leaving the ammonium chloride.

The amide may also be obtained by dehydrating the ammonium salt of the acid. Prepare a quantity of ammonium acetate by neutralising 50 g. glacial acetic acid with solid ammonium carbonate. Melt and pour the mass carefully into a small distilling flask, insert a thermometer dipping into the liquid, and distil, using a plain tube as condenser. The yield is improved by a preliminary heating for 6 hours at 220° in sealed tubes. Collect the fraction from 180–230°, which on cooling will give crystals of acetamide. These may be redistilled, or the odour of mouse excrement may be removed by crystallising from dry ether. M.p. 82°, b.p. 223°.

The amides are slowly hydrolysed by water, forming the ammonium salts of the acids, and are decomposed by boiling with alkalis, ammonia being set free. The hydrogen of the amino-group is readily replaced by chlorine or bromine to give the chloro- or bromo-amide (Hofmann's reaction, **214**).

213. Acetonitrile (Cyanomethane), CH_3CN. Further dehydration of the amide yields the cyanide, or nitrile :

$$CH_3CO\,.\,NH_2 - H_2O \rightleftharpoons CH_3CN.$$

This may be done by means of phosphoric anhydride, which retains the water in a non-volatile form as meta- or pyro-phosphoric acid, from which the nitrile is easily distilled.

In a small distilling flask place 15 g. of phosphorus pentoxide and 10 g. of dry acetamide, and mix well by shaking. Connect the flask to a small condenser, and heat the mixture carefully with a luminous flame, slowly at first with the burner in the hand until all frothing ceases, and then more strongly until the nitrile has all passed into the receiver. Mix the distillate with about half its volume of concentrated potash solution, and after shaking allow to settle and separate the upper layer. Distil again from a little pentoxide.

Nitriles are also obtained on distilling the corresponding alkyl iodide with potassium cyanide (192).

Acetonitrile is a colourless liquid of pleasant odour, sparingly soluble in water, b.p. 81·5°, sp. gr. ·790.

Reactions. 1. The nitrile is hydrolysed slowly by water, rapidly by alkali, liberating ammonia :

$$CH_3C \vdots N + H_2O \rightarrow CH_3CO\,.\,NH_2.$$

$$CH_3CONH_2 + KOH \rightarrow CH_3COOK + NH_3.$$

2. Reducing agents convert the nitrile into a primary amine by adding four hydrogen atoms to the triple bond :

$$CH_3C \vdots N + 4H \rightarrow \underset{\text{Ethylamine}}{CH_3CH_2\,.\,NH_2}.$$

214. Methylamine hydrochloride, $CH_3\,.\,NH_2\,.\,HCl$. By the action of alkali hypobromites * or hypochlorites upon the acid amides, the primary amine having one C atom less in the molecule is obtained (Hofmann's reaction).

An apparatus like that used for ethyl bromide is convenient, the flask being of 1 l. capacity. A thermometer also should be

* Hofmann, *Berichte*, **14**, 2725 (1881).

inserted as well as the tap-funnel, the bulb to be in the liquid. In this litre flask a solution of 50 g. KOH in about 100 c.c. water is placed, and heated to 60–70° on a sand-bath. Meanwhile 20 g. dry acetamide and 55 g. (18 c.c.) bromine are mixed carefully in a flask or beaker, placed in the fume chamber, and to the product, which consists of acetobromoamide, a solution of 20 g. KOH in 200 c.c. water is slowly added, keeping the mixture cool. This forms methyl-isocyanate :

$$CH_3 . CO . NH_2 + Br_2 = CH_3 . CO . NHBr + HBr,$$
$$CH_3 . CO . NHBr + KOH = CH_3 . N : CO + KBr + H_2O.$$

The liquid should now be of a bright yellow colour. If not, add a little more KOH, and then run the whole gradually through the tap-funnel into the strong KOH solution in the distilling flask, taking care that the temperature does not exceed 70–75°. Now raise the temperature gradually, after adding some broken pieces of pipe stem, and distil, collecting the methylamine (and a little NH_3) in the receiver, which contains a mixture of 50 c.c. conc. HCl and 50 c.c. water. When the distillate is no longer alkaline, evaporate the solution of the chlorides to dryness on the water-bath, and extract the $CH_3NH_2 . HCl$ with absolute alcohol, from which it crystallises :

$$CH_3 . N : CO + 2KOH = CH_3NH_2 + K_2CO_3.$$

215. Chloroacetic acid, $Cl . CH_2 . COOH$. The hydrogen atoms of the methyl group in acetic acid can be replaced successively by chlorine, giving mono-, di- and tri-chloroacetic acid.

In a weighed 250 c.c. retort, place 100 c.c. of glacial acetic acid and 8 g. of red phosphorus, and weigh the retort and contents. Fit the retort to a reflux condenser and arrange the apparatus near a window to receive as much light as possible. Heat the retort in a bath of boiling water and pass in dry chlorine until an increase in weight corresponding with monochloroacetic acid has been obtained.

$$\underset{60\text{ g.}}{CH_3 . COOH} \rightarrow \underset{94{\cdot}5\text{ g.}}{CH_2Cl . COOH}.$$

The reaction will occupy from 24 to 48 hours. Absorb the excess of chlorine with lime or caustic soda.

When the reaction is complete, distil the product from the retort, collecting the portion between 150° and 200° in a beaker. Cool the beaker rapidly, rubbing the sides with a glass rod until crystallisation sets in.

Filter the crystals by suction (Fig. 14) and redistil them. Collect the fraction between 180° and 190°.

Monochloroacetic acid is manufactured by passing chlorine through hot glacial acetic acid containing acetic anhydride. It forms colourless deliquescent crystals; m.p. 63°, b.p. 186°, sp. gr. 1·4. It is readily soluble in water, forming a solution which is more strongly acid than acetic acid. Great care should be taken when handling the acid owing to its severe action on the skin.

REACTIONS. 1. A solution of monochloroacetic acid decomposes when boiled, the chlorine being replaced by hydroxyl to form hydroxyacetic or glycollic acid. The replacement of chlorine is more rapid and complete if caustic alkali or silver oxide be used :

$$CH_2Cl \cdot COOH + H_2O = CH_2OH \cdot COOH + HCl.$$

$$CH_2Cl \cdot COOH + AgOH = CH_2OH \cdot COOH + AgCl.$$

2. Ferric chloride added to a neutral solution produces a dark brown colour, and when boiled this gives a reddish brown ppt. of the basic ferric salt. To detect chlorine in this (distinction from formate, acetate and glycine) filter and wash until free from chloride (the ppt. may be brought down with solution of ferric sulphate or iron alum instead of ferric chloride), boil a portion with a little NaOH solution, acidify the filtrate with HNO_3, and add $AgNO_3$. A white ppt. of AgCl confirms chloroacetic acid.

216. Aminoacetic acid (Glycine, Glycocoll, $NH_2 \cdot CH_2 \cdot COOH$). The chlorine atom in chloroacetic acid may also be replaced by the amino-group, NH_2, giving aminoacetic acid :

$$CH_2Cl \cdot COOH + 2NH_3 = CH_2NH_2 \cdot COOH + NH_4Cl.$$

Place 600 c.c. of ammonia solution of sp. gr. ·907 in a wide-mouthed bottle containing a stirrer (Fig. 11). Slowly run in from a tap-funnel a solution of 50 g. of monochloroacetic acid

in 50 c.c. of water, stirring all the time. Allow the mixture to stand for 24 hours, transfer it to a flask, drive off the excess of ammonia by passing a current of steam, and evaporate the liquid to a small bulk. Add copper carbonate in slight excess and filter. Evaporate till crystallisation of the copper salt commences, and allow to cool. Evaporate the filtrate until more crystals are obtained. Filter, dissolve the copper salt in water, precipitate the copper with sulphuretted hydrogen, filter and evaporate the filtrate to crystallise the aminoacetic acid.

An alternative method * is to prepare the copper salt of chloroacetic acid first. The same quantity may be used (50 g.) and the temperature of the water (120 c.c.) should not exceed 40°. After neutralising with copper carbonate, filter the solution and wash the residue with a little cold water (20 c.c. twice). To the filtrate add 250 c.c. of 9 per cent. aqueous ammonia, allow to stand for twenty-four hours at room temperature, then boil under reflux for three hours, concentrate and complete the preparation as above. Compare the yields of the copper salt and of glycine obtained by the two methods.

Aminoacetic acid forms large monoclinic crystals; m.p. 232–236°. It is very soluble in water and only slightly soluble in alcohol and ether.

Reactions. 1. To an aqueous solution of glycine add a drop of copper sulphate solution. A deep blue solution of the copper salt is formed.

2. To a solution add nitrous acid. Nitrogen is liberated and hydroxyacetic acid formed.

3. To a solution add ferric chloride. A deep red colour is produced, and on boiling this yields a brown ppt. of the basic ferric salt. This precipitate, when dissolved in dilute HCl and treated with HNO_2, liberates nitrogen (distinction from formate, acetate and chloroacetate).

217. Acetone (Propanone; Dimethylketone) $CH_3 . CO . CH_3$. Acetone is the only commonly occurring ketone. It was formerly obtained from pyroligneous acid, the aqueous distillate from

* H. Krause, *Chem. Ztg.* **55**, 666 (1931).

wood, which contains about 0·1 per cent. It is now manufactured by passing acetic acid vapour over heated metallic oxides (ThO_2, MnO, CaO) at 200°–300° ; or by passing alcohol vapour with excess of steam over a catalyst containing iron and calcium :

$$2C_2H_5OH + H_2O = CH_3COCH_3 + 4H_2 + CO_2$$

the residual gas after scrubbing contains 70–80 per cent. of hydrogen and is used for hydrogenation of unsaturated products, such as crotonaldehyde (207).

By the fermentation of starches with Fernbach's bacteria, 15–20 per cent. of the starch is converted into acetone. The Weizmann bacterial process uses a wider range of materials and gives a better yield of acetone, though in both cases *n*-butyl alcohol is the chief product : this is used for making butyl esters.

Acetone is a colourless mobile liquid with an agreeable smell. B.p. 56·3° ; sp. gr. ·8144 at 0°. It is very inflammable and mixes in all proportions with alcohol, ether and water.

Reactions. 1. To an aqueous solution of acetone add a little iodine solution and then sodium hydroxide until the colour of the iodine is nearly destroyed. Iodoform is produced at once, in the cold (189, 5).

2. To an aqueous solution of acetone add a freshly prepared solution of sodium nitroprusside and make alkaline with sodium hydroxide. A ruby red coloration is produced (Legal's test).

3. To a strong aqueous solution of acetone add a freshly prepared strong solution of sodium bisulphite. A white crystalline bisulphite compound, $(CH_3)_2C(OH) . SO_3 . Na$, is precipitated. The acetone can be recovered from this by distilling with alkali carbonate.

218. Acetoxime, $(CH_3)_2C : N . OH$. Dissolve 3 g. of sodium hydroxide in 20 c.c. of water in a small flask, cool well, and add 5 g. of hydroxylamine hydrochloride. To this add now 6 g. of pure acetone, mix well by gentle shaking, cork the flask and allow to stand in the cold for 24 hours. Acetoxime crystallises, but it is best extracted with ether. Test the liquid first for free hydroxylamine, by boiling with Fehling's solution. There should be none. Extract the mixture with an equal volume of ether. Repeat this twice, and filter the whole ethereal extract through a dry filter.

Distil off the ether from a water-bath, and pour the residue into a small flask to crystallise.

Acetoxime crystallises in colourless needles, melting at 69°. On boiling with dilute acid it is hydrolysed, liberating hydroxylamine, which reduces Fehling's solution.

219. Glycol (Ethanediol), $CH_2OH \cdot CH_2OH$. Dihydroxy derivatives of the paraffins are called glycols. They can be obtained by the oxidation of olefines, the simplest being ethylene glycol ; the reaction proceeds better in alkaline solution :

$$3CH_2 : CH_2 + 2MnO_4' + 4H_2O = 3CH_2OH \cdot CH_2OH + 2MnO_2 + 2OH'.$$

Glycol is obtained from ethylene also by first preparing the chlorohydrin by union with hypochlorous acid (dilute chlorine water), and then hydrolysing this with sodium carbonate :

$$CH_2 : CH_2 + HOCl \rightarrow CH_2OH \cdot CH_2Cl \xrightarrow[\text{soln.}]{Na_2CO_3} CH_2OH \cdot CH_2OH.$$

Ethylene glycol is a colourless viscous liquid of sp. gr. 1·125 and b.p. 197·5°. It has a sweet taste and is miscible with water and alcohol. It gives a mono- and a di-sodium derivative, and yields both organic and inorganic ethereal salts. The diacetate, $(CH_2 \cdot OCOCH_3)_2$, is a useful solvent ; the dinitrate, $CH_2O \cdot NO_2 \cdot CH_2O \cdot NO_2$, is a powerful explosive.

Glycol, acetaldehyde, or ethylene can be oxidised to the dialdehyde, glyoxal, by means of selenium dioxide, SeO_2* :

$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + O_2 \rightarrow \begin{matrix} CHO \\ | \\ CHO \end{matrix} + 2H_2O.$$

Glyoxal is important in the synthesis of tartaric acid (225).

220. Glycerol, $C_3H_5(OH)_3$, occurs in the natural fats and oils in combination with certain higher fatty acids, chiefly palmitic and stearic acids. The fats are thus glycerol esters, and may be hydrolysed by heating with water or with sulphuric acid under

* Riley and Friend, *J.C.S.*, 1932, 2342.

pressure, or by boiling with alkali in the process of soap manufacture.

Soaps are the sodium salts (hard soaps) or potassium salts (soft soaps) of the acids occurring in the natural fats and oils, from which they are prepared by the action of the caustic alkalis. Chemically, the process is similar to that used in the hydrolysis of ethyl acetate, and is known as saponification.

Weigh out 100 g. of beef suet or palm oil, place in a large porcelain dish with half its bulk of water, and warm until melted. Add 20 g. of caustic soda dissolved in 100 c.c. of water, and boil gently with frequent stirring, or blow steam into the liquid, until the mixture is homogeneous, and all fat has disappeared. Now add 200 c.c. of a saturated solution of common salt, stir well, and set aside to cool. The soap will separate as a firm curd on the surface, and may be removed with a spatula.

$$\underset{\text{Glycerol palmitate (Palmitin)}}{(C_{15}H_{31}COO)_3C_3H_5} + 3NaOH = \underset{\text{Sodium palmitate}}{3C_{15}H_{31}COONa} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}.$$

The lye or liquor left after the removal of the curd is an aqueous solution of glycerol and salt together with free alkali. After a purifying treatment the liquor is evaporated under reduced pressure to recover the salt; the glycerol is then distilled with superheated steam and the distillate again evaporated in vacuo.

Pure glycerol is a colourless solid of m.p. 20°, but is usually met with as a sweet viscous hygroscopic liquid; b.p. 290°, sp. gr. 1·24. It decomposes slightly near its boiling point, giving off acrolein.

$$CH_2OH \,.\, CHOH \,.\, CH_2OH = CH_2 : CH \,.\, CHO + 2H_2O.$$

Glycerol is miscible with water and alcohol in all proportions, but is insoluble in ether.

REACTIONS. 1. Heat a drop of glycerol with twice its weight of potassium hydrogen sulphate. Acrolein is given off and can be recognised by its smell.

2. Dip a borax bead in glycerol and heat in a bunsen flame. The flame is coloured green by the boric acid.

3. A 1 per cent. solution of borax is coloured pink by a few drops of phenolphthalein solution. On adding glycerol, the pink

colour disappears, but reappears on warming. Other polyvalent alcohols and sugars give this reaction. The hydroxyl groups of the alcohols condense with the boric acid to form much stronger acids, which hydrolyse on warming the solution.

Glycerol is used to some extent in pharmacy, but chiefly in the manufacture of nitroglycerine (glycerol trinitrate).

221. Oxalic acid, $(COOH)_2 2H_2O$. Sodium oxalate, from which the acid and other compounds can be obtained, is now manufactured from sodium formate by heating to 300–400°, when hydrogen is liberated :

$$2H \cdot COONa = (COONa)_2 + H_2.$$

The acid was formerly manufactured by oxidation of wood sawdust. It may also be obtained from many carbohydrates by oxidising with nitric acid.

In a large beaker place 100 c.c. conc. nitric acid, and 30 g. powdered cane sugar. Cover with a clock glass and heat gently on a water or steam bath, in the fume chamber, until the reaction sets in. Abundant red fumes are evolved. When the first violent reaction is over, evaporate in the fume chamber to about 30 c.c. and allow to cool. Oxalic acid crystallises in long monoclinic prisms, which should be drained on a small porcelain funnel and recrystallised from a little hot water.

The acid forms colourless prisms, containing two molecules of water of crystallisation. The crystals melt at 101·5°, losing their water, and the anhydrous acid sublimes slowly, melts at 189°, and decomposes at higher temperatures into carbon dioxide and formic acid.

Reactions. 1. Heated with concentrated sulphuric acid, oxalates decompose, without charring, into carbonic oxide, carbon dioxide, and water (compare 205, 1).

$$H_2C_2O_4 = CO + CO_2 + H_2O.$$

2. To a neutral solution of an oxalate add calcium chloride ; a white crystalline precipitate of calcium oxalate, CaC_2O_4, is formed, insoluble in ammonia or dilute acetic acid.

3. To a solution of oxalic acid or a salt add dilute sulphuric

acid and a little potassium permanganate, and warm gently. The permanganate is reduced and decolorised, and the oxalic acid oxidised to carbon dioxide and water.

$$H_2C_2O_4 + O = 2CO_2 + H_2O.$$

222. Succinic acid, $(CH_2COOH)_2$, occurs in amber, and may be obtained by distilling this. It is made from ethylene dibromide, through the cyanide, which is hydrolysed :

$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} \xrightarrow[2KCN]{} \begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} \xrightarrow[4H_2O]{} \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH. \end{array}$$

The acid crystallises in colourless monoclinic prisms or plates, melting at 182°. Heated quickly to about 235°, it forms the anhydride,

$$\begin{array}{l} CH_2 . CO \\ | \qquad\quad > O, \\ CH_2 . CO \end{array}$$

which melts at 119·6° and boils at 261°.

REACTIONS. 1. The calcium, lead and silver salts are thrown down as white ppts. from strong solutions of neutral succinates.

2. Ferric chloride gives a bulky brown ppt. of basic ferric succinate, $(C_4H_4O_4)_3Fe_2 . Fe_2O_3$, which on boiling with ammonia forms ammonium succinate partly or completely, leaving $Fe(OH)_3$. On adding $BaCl_2$ and alcohol to the filtrate, a white ppt. of barium succinate is obtained (distinction from benzoates).

3. Heat a small crystal of succinic acid or anhydride gently with twice its bulk of resorcinol and a pellet of fused zinc chloride. A dark red mass is obtained. When cool, dissolve in a little caustic soda and pour into cold water. A fine greenish yellow fluorescence is shown (succineine). Compare fluorescein, 289.

223. Glycollic acid (Hydroxy-acetic acid), $CH_2OH . COOH$, may be obtained by the hydrolysis of chloroacetic acid, or by the action of nitrous acid on glycine :

$$CH_2ClCOONa + NaOH = CH_2OH . COONa + NaCl.$$
$$CH_2NH_2COOH + HNO_2 = CH_2OH . COOH + N_2 + H_2O.$$

It is one of the oxidation products of glycol, and of fructose, and occurs in unripe grapes. It forms colourless crystals of m.p. 80°, readily soluble in water.

224. Lactic acid (*a*-Hydroxypropionic acid), $CH_3CHOHCOOH$. This acid may be prepared by boiling α-chloro- or α-bromo-propionic acid with water, or by warming these with silver oxide. It may also be obtained from acetaldehyde, by hydrolysis of its cyanohydrin :

$$CH_3CHO \xrightarrow[HCN]{} CH_3CHOH \,.\, CN \xrightarrow[H_2O]{} CH_3CHOH \,.\, COOH$$

It is manufactured by the lactic fermentation of glucose, lactose or cane sugar :

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_3H_6O_3.$$

Pure anhydrous lactic acid is a crystalline solid of m.p. 18°, but the commercial pure lactic acid (75 per cent.) is a colourless syrupy liquid with a sour smell and taste. Prepared as above lactic acid is optically inactive, but can be resolved into a dextro- and a laevo-form. Since only the *d*-form is metabolised when the acid is used in foods, the *l*-form being mainly rejected, it is of interest that certain ferments convert glucose into *d*-lactic acid to the extent of 90–95 per cent.* The dextro-form is found in muscle and is known as para- or sarco-lactic acid. Lactic acid is used in dyeing and printing.

REACTIONS. 1. Lactic acid solutions decolorise $KMnO_4$ slowly in the cold, rapidly on warming, evolving CO_2 and some acetaldehyde.

2. $SnCl_2$ solution just cleared with HCl gives with solutions of lactates a white crystalline ppt. of basic stannous lactate :

$$(CH_3CHOH \,.\, COOSn)_2O.$$

3. Lactic acid, distilled with an equal bulk of conc. H_2SO_4 diluted with twice its volume of water, decomposes into acetaldehyde and formic acid.

$$CH_3CH(OH)COOH + H_2O \rightarrow H \,.\, COOH + CH_3CH(OH)_2$$
$$\rightarrow CH_3CHO + H_2O.$$

* Tatum and Peterson, *Ind Eng. Chem.* **27**, 1493 (1935).

These can be detected in the distillate by means of ammoniacal silver and $HgCl_2$ respectively.

4. The acid may be converted into the zinc or calcium salt and this examined under the microscope. The zinc salt,

$$Zn(C_3H_5O_3)_2 \,.\, 3H_2O,$$

forms clusters of colourless, quadratic prisms, which are very characteristic.

225. Tartaric acid, $(CHOH \,.\, COOH)_2$. Tartaric acid is manufactured chiefly from argol, the acid potassium salt, which crystallises in wine vats. It is now made also from glycol (219) through glyoxal and the cyanohydrin, which is hydrolysed :*

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{SeO_2} \begin{array}{l} CHO \\ | \\ CHO \end{array} \xrightarrow{2HCN} \begin{array}{l} CH(OH)CN \\ | \\ CH(OH)CN \end{array} \xrightarrow{4H_2O} \begin{array}{l} CH(OH)COOH \\ | \\ CH(OH)COOH. \end{array}$$

The acid crystallises in large monoclinic prisms, readily soluble in water or alcohol. The synthetic acid is inactive (racemic) ; that made from argol is dextro-rotatory. Heated rapidly, the acid melts at 167–170°, and then chars, as do the salts, and evolves vapours smelling of burnt sugar. The vapour contains pyruvic acid, acetaldehyde, acetone, formic and acetic acids, and oxides of carbon. Charring also occurs on heating with concentrated sulphuric acid.

REACTIONS. 1. To a neutral solution of a tartrate add calcium chloride solution, cool and shake well. Crystalline calcium tartrate separates, soluble in acetic acid, insoluble in ammonia.

2. To a neutral solution of a tartrate add silver nitrate : a white crystalline precipitate of silver tartrate is formed. This is soluble in ammonium hydroxide, and the solution on warming gives a mirror of metallic silver.

3. To a solution of tartaric acid add some saturated solution of potassium chloride, cool and shake : a white crystalline precipitate of potassium hydrogen tartrate, $KC_4H_5O_6$, is obtained.

Potassium hydrogen tartrate (Cream of Tartar), $K \,.\, H \,.\, C_4H_4O_6$. This salt is deposited, in the form of argol, during the fermentation

* Newman and Riley, *J.C.S.*, 1933, 45.

of grape juice. It is nearly insoluble in alcohol, and while readily soluble in hot water, requires sixty parts of cold water. The commercial cream of tartar is made by purifying crude argol.

Dissolve 20 g. of tartaric acid in 100 c.c. of warm water, and filter if necessary. Carefully neutralise one half with a clear solution of about 9 g. caustic potash in 50 c.c. water. This liquid now contains normal potassium tartrate, $K_2C_4H_4O_6$. Heat to boiling, and add the other half of the tartaric acid solution, also heated, and set aside in a covered beaker to crystallise. Yield, about 20 g.

Potassium sodium tartrate (Rochelle Salt),

$$K . Na . C_4H_4O_6 . 4H_2O.$$

Mix 20 g. potassium hydrogen tartrate with 300 c.c. water in a flask, and while warming add gradually a solution of 15 g. crystallised carbonate of soda, until the tartrate is completely dissolved and the solution exactly neutralised. If too much soda is introduced, add a little more of the bitartrate. Filter the hot neutral liquid and concentrate. Rochelle salt crystallises in colourless transparent prisms. Yield, about 20 g.

The salt is readily soluble in water, and in taste resembles common salt. It is used in medicine as a mild laxative. Heated in a dry tube, it first loses the water of crystallisation and then chars. For reactions see Tartaric Acid (above).

Potassium antimonyl tartrate (Tartar Emetic),

$$K(SbO)C_4H_4O_6 . \tfrac{1}{2}H_2O.$$

In a 500 c.c. round flask place 20 g. cream of tartar and an equal weight of antimony oxide. Add 400 c.c. of water, and boil gently until no more of the oxide will dissolve, and the liquid no longer contains the acid salt. Add water from time to time to keep to the original volume. Filter hot. On cooling, small colourless rhombic octahedra of the double salt crystallise.

These lose their water of crystallisation on exposure to air, and crumble to powder.

Tartar emetic is soluble in 14 parts of water at 10°. The solution has an unpleasant metallic taste. With sulphuretted hydrogen in presence of hydrochloric acid the antimony is precipitated as

orange-red antimony trisulphide. The substance is used as a mordant in cotton dyeing, and in medicine. In small doses of ·1 to ·7 of a grain its action is sudorific, but in larger doses of 1–3 grains it acts as an emetic. An excess is poisonous.

226. Citric acid, $C_6H_8O_7 . H_2O$, occurs in many fruits, and is prepared from lemon juice, which contains 6 or 7 per cent. Milk of lime precipitates the calcium salt, which is then decomposed with sulphuric acid.

The acid crystallises in large rhombic prisms with one molecule of water of crystallisation. It is soluble in 4 parts of water at 20°, and easily soluble in alcohol. The anhydrous acid is formed at 55° and melts at 160°, and at higher temperatures darkens and decomposes.

REACTIONS. 1. Heated with concentrated sulphuric acid, citrates evolve carbon monoxide and carbon dioxide, and are slowly blackened.

2. Calcium chloride in neutral solutions gives no precipitate in the cold, but on boiling, a white, crystalline precipitate of calcium citrate, $Ca_3(C_6H_5O_7)_2 4H_2O$, is produced.

3. Silver nitrate gives with neutral solutions of citrates a white, curdy precipitate of silver citrate, $C_3H_5O . (COOAg)_3$. This is soluble in ammonia, but is reduced only after long-continued boiling.

CARBOHYDRATES

227. The group of carbohydrates includes the various forms of starch and of cellulose, which are insoluble in cold water, and a great variety of sugars, which are soluble. A few examples of these follow.

Starch, $(C_6H_{10}O_5)_n$. Starch is found as small granules in the cells of grain, potatoes, and legumes. The granules from different sources vary in appearance and also in size, the rice granules having a diameter of about ·005 mm. and those from potatoes ·07 mm.

Starch is insoluble in cold water, alcohol, and ether. When heated with water it forms a gelatinous liquid called starch paste

It is hydrolysed by boiling with acids, and gives glucose as a final product, but the commercial glucose usually contains maltose and dextrin, which are intermediate. Starch is not directly fermentable by yeast, but is converted by diastase, an enzyme present in the yeast, into maltose, which is further hydrolysed and fermented.

REACTIONS. 1. Heat a little starch in a dry tube. It chars, gives off water, acetic acid, etc., and leaves charcoal.

2. To a dilute solution of starch paste add a trace of free iodine. A blue colour is produced which disappears on warming to about 80°, but returns on cooling.

3. For the hydrolysis of starch, see **230.**

228. Cane sugar (Sucrose), $C_{12}H_{22}O_{11}$. Cane sugar crystallises in anhydrous monoclinic prisms, m.p. 160°. Its solution in water is dextrorotatory. When boiled the solution is slowly hydrolysed, fructose (laevorotatory) and glucose (dextrorotatory) being produced.

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}.$$

Since the laevorotation of fructose is greater than the dextrorotation of glucose, the resulting mixture is laevorotatory, and is called " invert " sugar. The process is commonly called " inversion," this term being applied also to other cases of hydrolysis of bioses. The hydrolysis is accelerated by the presence of an acid, and the acceleration is greater the greater the degree of dissociation of the acid. It is attributed to the catalytic action of hydrogen ions (85).

Cane sugar is not directly fermentable by yeast, but the enzyme *invertase* present in yeast " inverts " it, and another enzyme, *zymase*, also present in the yeast-cell, induces alcoholic fermentation of both the hexose sugars. Cane sugar in a similar way can be fermented to give lactic and butyric acids (see lactic acid, 224).

REACTIONS. 1. Heat a little sugar in a dry tube. It melts, turns yellow (caramel), chars, giving off water, acetic acid, acetone, etc., and leaving charcoal.

2. Heat a solution of sugar with a few drops of dilute sulphuric

acid. The product, when neutralised, is readily fermentable by yeast, and reduces Fehling's solution. Cane sugar does not reduce Fehling's solution (see grape sugar, 230, 3).

3. Heat a little sugar with conc. sulphuric acid. Charring occurs, and carbon dioxide and sulphur dioxide are evolved.

4. Warm some sugar with conc. nitric acid. Copious reddish brown fumes are evolved, the sugar being oxidised to oxalic and other acids.

229. **Milk sugar** (Lactose), $C_{12}H_{22}O_{11} + H_2O$. Milk sugar occurs in the milk of all mammals, in quantities which vary in different species. It is obtained by concentrating the whey, the liquid remaining after separating the casein in cheese-making. It forms rhombic crystals, less soluble in water than cane sugar. The solution has a slightly sweet taste, and is dextrorotatory. It reduces Fehling's solution, though to a less degree than grape sugar, and reduces ammoniacal silver solutions rapidly on warming. It is hydrolysed by certain enzymes (*lactase*) or by boiling with dilute acids, into glucose and galactose. Under the influence of certain ferments (224) it is converted into lactic acid, and the souring of milk is due to this fermentation. Unlike cane sugar, lactose yields with phenylhydrazine, a phenyl-lactosazone melting at 200°.

Maltose, $C_{12}H_{22}O_{11}$, is the soluble sugar produced in germinating seeds by the action of *diastase* on starch, and is manufactured by the action of malt on starch. A similar change is effected by boiling the starch with dilute acids, and the maltose is further hydrolysed into glucose either by the continued action of the acid, or by the enzyme *maltase*. Maltose is usually present in commercial grape sugar, together with dextrin.

It crystallises in fine, colourless needles, easily soluble in water. The solution is dextrorotatory, reduces Fehling's solution and ammoniacal silver on warming, and is fermentable with yeast. The osazone forms clusters of thin, yellow prisms, melting at 206°.

230. **Grape sugar** (Glucose) from Starch. Mix 20 g. of potato starch to a thin cream with cold water, and pour this into about a

litre of boiling water contained in a large flask. Transfer about 100 c.c. to each of two smaller flasks and allow to cool to 30–40°. To the main portion add 5 c.c. dil. sulphuric acid and boil gently on a sand-bath until a few drops of the liquid, diluted with water in a test-tube, give no blue (starch) or brown (dextrins) colour with a drop of iodine solution. The starch is then completely hydrolysed into grape sugar.

$$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6.$$

Neutralise the sulphuric acid with chalk, filter and evaporate to dryness on the steam-bath.

To the two smaller portions of starch solution add respectively a little diastase and a little aqueous extract of crushed malt, which contains diastase. Trace the change into grape sugar as above, and then add to the filtered main portion and evaporate.

Reactions. 1. Heated in a dry tube, grape sugar melts readily (147°), loses water, then chars, evolving combustible gases with an odour of burnt sugar, and leaving a residue of carbon.

2. Heated with conc. sulphuric acid, the mixture turns yellow, then brown, afterwards charring and evolving sulphur dioxide and carbon dioxide.

3. Grape sugar reduces Fehling's solution on warming, giving a red precipitate of cuprous oxide. (Distinction from cane sugar.) See the estimation of sugars (481).

4. Ammoniacal silver is also reduced, giving a silver mirror.

5. The fermentation test for sugars (189) may be applied in a test-tube or small flask, and the evolution of CO_2 demonstrated.

6. When a solution of glucose is mixed with a solution of phenylhydrazine acetate (or hydrochloride + sodium acetate), and warmed for a short time on the water-bath, a yellow crystalline precipitate of glucosazone is obtained :

$$\begin{aligned} CH_2OH(CHOH)_4CHO + 3H_2N \cdot NH \cdot Ph \\ = CH_2OH(CHOH)_3 \cdot \underset{\displaystyle CH : N \cdot NH \cdot Ph}{\overset{\displaystyle C : N \cdot NH \cdot Ph}{|}} \\ + Ph \cdot NH_2 + NH_3 + 2H_2O. \end{aligned}$$

This may be recrystallised from hot water, and melts at 209°.

CYANOGEN DERIVATIVES

231. Potassium ferrocyanide (Yellow Prussiate of Potash), $K_4Fe(CN)_6 . 3H_2O$. This salt is the starting substance for the preparation of most of the cyanogen compounds. It was formerly prepared by igniting carbonised nitrogenous animal matter (horn and leather shavings, hoofs, blood, etc.) with crude potash and iron. Ferrocyanides are now produced in various ways from the hydrocyanic acid in crude coal gas.

It may be obtained by adding a solution of pure ferrous sulphate to one of potassium cyanide until a slight permanent precipitate is produced. Heat to boiling, filter and evaporate the clear filtrate. On cooling, potassium ferrocyanide crystallises in large yellow monoclinic prisms, with three molecules of water of crystallisation. This water is expelled on heating to 100°, and the crystals disintegrate to a white powder.

$$FeSO_4 + 2KCN = Fe(CN)_2 + K_2SO_4,$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Ferrocyanides of the alkalis, alkaline earths and magnesium are soluble in water, the barium salt being sparingly soluble. Those of the heavy metals are insoluble in water. The sodium salt, $Na_4Fe(CN)_6 . 10H_2O$, is now manufactured largely instead of the potassium salt, and by similar methods. It crystallises from water in large yellow monoclinic prisms, which are efflorescent and lose all the water at 100°.

Dry Reactions. 1. Heated alone, potassium ferrocyanide decomposes into cyanide, nitrogen and a carbide of iron :

$$K_4Fe(CN)_6 = 4KCN + N_2 + FeC_2 (\text{or } Fe + 2C).$$

2. Heated with conc. sulphuric acid, carbon monoxide is evolved (see preparation of this, **107, 3**).

Reactions in Solution. $[Fe(CN)_6]''''$. 1. **Silver nitrate** precipitates white silver ferrocyanide, $Ag_4Fe(CN)_6$, insoluble in dilute acids or NH_4OH, soluble in potassium cyanide.

2. **Copper sulphate** produces a brown ($CuK_2Fe(CN)_6$) or chocolate ($Cu_2Fe(CN)_6$) precipitate, according to the proportions employed.

3. **Ferrous salts** give a white precipitate of potassium ferrous ferrocyanide, which is quickly oxidised to the blue ferric salt:

$$3FeSO_4 + 2K_4Fe(CN)_6 = Fe_3K_2[Fe(CN)_6]_2 + 3K_2SO_4.$$

Owing to this oxidation the usual precipitate is of a light-blue colour.

4. **Ferric salts** give a dark-blue precipitate of Prussian blue, ferric ferrocyanide,

$$4FeCl_3 + 3K_4Fe(CN)_6 = Fe_4[Fe(CN)_6]_3 + 12KCl.$$

These precipitates are insoluble in dilute acids, but are decomposed by caustic alkalis, forming the alkali ferrocyanide and ferrous or ferric hydroxide.

$$Fe_3K_2[Fe(CN)_6]_2 + 6KOH = 2K_4Fe(CN)_6 + 3Fe(OH)_2.$$

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 3K_4Fe(CN)_6 + 4Fe(OH)_3.$$

232. Potassium ferricyanide (Red Prussiate of Potash),

$$K_3Fe(CN)_6.$$

By oxidation of the iron in ferrocyanide, the latter passes into ferricyanide of potassium. This may be effected by passing chlorine gas into a solution of potassium ferrocyanide until the liquid is dark red in colour, and a drop no longer gives a blue coloration with a drop of ferric chloride. The liquid now contains potassium ferricyanide and chloride.

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl.$$

On evaporating the clear liquid the ferricyanide crystallises in red rhombic prisms.

Another method consists in oxidising the ferrocyanide by boiling with freshly prepared lead peroxide. 25 g. potassium ferrocyanide is dissolved in 400 c.c. water, 10 g. of lead peroxide mixed to a paste with water added, and the mixture is boiled on a sand-bath until no trace of ferrocyanide can be detected in a filtered portion of the liquid, after acidifying with dilute hydrochloric acid. The liquid is now strongly alkaline owing to the

formation of caustic potash, which dissolves some of the lead monoxide.

$$2K_4Fe(CN)_6 + PbO_2 = 2K_3Fe(CN)_6 + K_2PbO_2.$$

Pass a stream of carbon dioxide through the liquid during the boiling until all the lead is precipitated, and filter. Crystallise the potassium ferricyanide as in the first method. Yield about 20 g.

Reactions in Solution. $[Fe(CN)_6]'''$. 1. **Silver nitrate** precipitates orange-coloured silver ferricyanide, $Ag_3Fe(CN)_6$, insoluble in dilute HNO_3, soluble in NH_4OH or KCN solution.

2. **Ferrous salts** give a dark-blue precipitate known as Turnbull's blue, which is identical with Prussian blue, ferric ferrocyanide. The insoluble blues are obtained in a pure state only in presence of excess of the iron salt. If the iron salt be added to an excess of alkali ferro- or ferri-cyanide, soluble blues are obtained which contain a variable amount of the alkali metal, according to the proportions used.

The ferricyanide rapidly changes to ferrocyanide, while the iron hydroxide is oxidised.

3. **Ferric salts** give only a brown coloration.

It will be observed that the iron contained in the acid radicals, or anions, of ferro- and ferri-cyanides is not precipitated by KOH, unlike the basic radical or cation. A method for the complete decomposition of complex cyanides will be found in par. **373**.

If it be desired to test for simple cyanides in a mixture containing ferro- and ferri-cyanides, or to remove the simple cyanides, the mixture may be distilled with excess of sodium bicarbonate, which decomposes cyanides but not the complex cyanides :

$$NaCN + NaHCO_3 = Na_2CO_3 + HCN.$$

The distillate is then examined for cyanide, and the residue for ferro- and ferri-cyanides.

233. Hydrocyanic acid, HCN. Cyanides of the alkali metals are readily soluble in water, those of the alkaline earths sparingly soluble, the solutions being alkaline in reaction. Those of the

heavy metals, except mercuric cyanide, $Hg(CN)_2$, are insoluble in water, but generally soluble in a solution of potassium cyanide. Most cyanides are decomposed by dilute acids, evolving hydrocyanic acid.

When heated alone, most heavy metal cyanides decompose, evolving the poisonous, combustible cyanogen gas. The alkali cyanides fuse on heating, and oxidise in air to cyanates. Heated with sulphur, potassium cyanide forms thiocyanate, KSCN, which produces a blood-red colour with ferric chloride. Hence the use of potassium cyanide as a reducing agent for oxides and sulphides.

Reactions in Solution. CN'. Use a solution of potassium cyanide.

1. **Silver nitrate** gives a white curdy precipitate of silver cyanide, AgCN, which dissolves until one molecule of silver nitrate has been added for each two molecules of potassium cyanide, forming the compound AgCN . KCN. The addition of more $AgNO_3$ produces a permanent precipitate of AgCN, which greatly resembles AgCl, being soluble in NH_4OH, $Na_2S_2O_3$, etc., and insoluble in dilute HNO_3. To distinguish and separate silver cyanide from the halide salts, ignite the dry precipitate; the cyanide decomposes, leaving metallic silver, which may be dissolved by conc. HNO_3; the halide salts fuse without decomposition, and AgCl may then be extracted with conc. NH_4OH.

2. Free HCN, liberated from KCN with a little dilute acid in a small beaker, decomposes yellow **ammonium sulphide** placed on the bottom of a watch-glass over the beaker, forming thiocyanate.

$$(NH_4)_2S_2 + HCN = NH_4SCN + NH_4SH.$$

This, when acidified with HCl to decompose the hydrosulphide, gives a deep-red colour with $FeCl_3$. This is a very delicate test for hydrocyanic acid.

3. To the solution of cyanide add a mixture of $FeSO_4$ and $FeCl_3$ solutions, and acidify with HCl to dissolve hydroxides of iron. A deep-blue precipitate, or a blue or green coloration of **Prussian blue**, is obtained. (See Ferrocyanic Acid).

234. Cyanic acid, HOCN. Salts of this acid, called cyanates, are produced by the oxidation of cyanides, as when these are used as reducing agents :

$$KCN + PbO = KOCN + Pb.$$

The acid itself is a tautomeric substance, forming derivatives of the two types :

$$\underset{\text{Cyanic acid}}{N \vdots C . OH} \quad \text{and} \quad \underset{\text{Isocyanic acid}}{H . N : C : O.}$$

Only one acid is known, and the first formula is assigned to it. Ammonium cyanate is obtained from the potassium salt and is used in the synthesis of urea (236) :

$$N \vdots C . ONH_4 \rightleftharpoons CO(NH_2)_2.$$

235. Thiocyanic acid, HSCN. Like cyanic acid, thiocyanic acid is a tautomeric substance, and although only one acid is known, two classes of derivatives are known, corresponding to the two forms :

$$\underset{\text{Thiocyanic acid}}{N \vdots C . SH} \quad \text{and} \quad \underset{\text{Isothiocyanic acid}}{H . N : C : S.}$$

The free acid is obtained by precipitating barium from the barium salt with sulphuric acid, or mercury from its salt with hydrogen sulphide. The acid polymerises readily, like cyanic acid, to a solid polymeride.

REACTIONS IN SOLUTION. SCN'. Use potassium or ammonium thiocyanate.

1. **Silver nitrate** produces a white curdy precipitate of silver thiocyanate, AgSCN, insoluble in dilute acids, soluble in NH_4OH.

2. **Copper sulphate,** to which sulphurous acid has been added, forms a white precipitate of cuprous thiocyanate, $Cu_2(SCN)_2$. On ignition this leaves cuprous sulphide, Cu_2S, and is employed as a means of estimating copper (474).

3. **Ferric salts** give a deep red coloration, owing to the formation of the soluble ferric thiocyanate, $Fe(SCN)_3$. The solution should be slightly acid. Free thiocyanic acid also gives the red colour, which is that of the unionised ferric salt, and provides a delicate test for the ferric ion. Ferrous salts give no colour.

Potassium thiocyanate, KSCN, is prepared by fusing potassium cyanide with sulphur. On cooling, the mass is extracted with water, the excess of sulphur removed by filtration, and the filtrate concentrated. The salt crystallises in colourless deliquescent prisms, very soluble in water with considerable absorption of heat. The solution has an alkaline reaction.

Ammonium thiocyanate, NH_4SCN, is prepared by boiling under reflux equal volumes of carbon bisulphide and conc. ammonium hydroxide :

$$CS_2 + 2NH_3 = NCS \,.\, NH_4 + H_2S.$$

It is similar to the potassium salt, and when heated to 165–170° is transformed into thiourea :

$$NCS \,.\, NH_4 \rightleftharpoons SC(NH_2)_2.$$

236. Urea, $CO(NH_2)_2$. Urea is readily produced by the addition of ammonia to carbonyl chloride (compare acetamide, 212). It is of interest as being the first organic substance to be synthesised. Wöhler, in 1828, obtained it by the action of heat on ammonium cyanate :

$$N \vdots C \,.\, ONH_4 \rightleftharpoons CO : (NH_2)_2.$$

The change is reversible : a dilute solution of urea at 100° contains some ammonium cyanate.*

It is now manufactured by the partial hydrolysis of cyanamide in feebly acid solution :

$$CaCN_2 \rightarrow H_2N \,.\, CN \rightarrow CO(NH_2)_2,$$

and also by heating a mixture of CO_2 and NH_3 to 130–150° at a pressure of 33–35 atmos. Ammonium carbamate is first formed :

$$CO_2 + 2NH_3 \rightarrow NH_2COONH_4 \rightarrow CO(NH_2)_2 + H_2O.$$

To prepare urea, heat 50 g. of potassium cyanide in an iron dish, and when fusion begins, add gradually, while stirring, 140 g. of red oxide of lead. Continue to heat, and when frothing ceases

* Walker and Hambly, *J.C.S.*, 1895, 746.

pour the melt on to an iron plate and allow to cool. Separate the impure cyanate from the lead and extract the cyanate with several small quantities of cold water. Transfer the extract to a beaker, add a concentrated solution of 25 g. of ammonium sulphate, and evaporate to dryness on a water-bath. Extract the urea from the residue by boiling with alcohol under a reflux condenser. Concentrate this extract after filtering, and allow the urea to crystallise.

Urea crystallises in colourless prisms, melting at 132°. It is very soluble in water, and reacts as a monacid base. In solution the tautomeric imino-form * is also present :

$$O:C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} \rightleftharpoons HO.C\begin{matrix}\diagup NH_2\\ \diagdown\!\!\diagdown NH\end{matrix}.$$

REACTIONS. 1. To a strong solution of urea, add a drop of conc. nitric acid. A white crystalline precipitate of urea nitrate, $CO:(NH_2)_2 . HNO_3$, is formed. The oxalate, $C_2H_2O_4(CON_2H_4)_2$, may also be precipitated by using a concentrated oxalic acid solution.

2. Melt a few crystals of urea in a porcelain dish and heat gently. Bubbles of ammonia are given off, and biuret is formed :

$$2CO:(NH_2)_2 = NH:(CONH_2)_2 + NH_3.$$

Cool, add a few drops of water, a drop of copper sulphate solution, and a few drops of caustic soda. A violet coloration is produced.

3. To a solution of urea, add sodium hypochlorite. Nitrogen is evolved :

$$CO:(NH_2)_2 + 3NaOCl = 2H_2O + CO_2 + N_2 + 3NaCl.$$

4. To a solution of urea, add a little nitrous acid solution. Nitrogen is evolved :

$$CO:(NH_2)_2 + 2HNO_2 = 3H_2O + CO_2 + 2N_2.$$

The last two reactions provide methods for the quantitative estimation of urea.

* E. A. Werner, *Chemistry of Urea*, Longmans, 1923.

5. Urea is hydrolysed by boiling with dilute mineral acids or alkali hydroxides, yielding ammonia :

$$CON_2H_4 + NaOH = NH_3 + NaOCN + H_2O.$$
$$NaOCN + 2H_2O = NH_3 + NaHCO_3.$$

The reaction is not reliable, however, for the estimation of urea.

237. Thiourea (Thiocarbamide), $SC(NH_2)_2$. The intramolecular change of ammonium thiocyanate into thiourea is similar to that of ammonium cyanate into urea, but takes place at a higher temperature. The change also is less complete, the equilibrium in the thio-compounds being nearer to the ammonium salt.

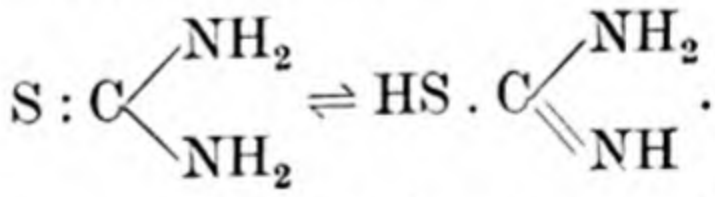
Thiourea forms colourless rhombic prisms, m.p. 172°, readily soluble in water and hot alcohol, sparingly soluble in cold alcohol or ether. It is hydrolysed by boiling with acid or alkali :

$$SC(NH_2)_2 + 2H_2O = 2NH_3 + CO_2 + H_2S.$$

It is converted into cyanamide in contact with oxides of lead, mercury or silver, even at ordinary temperatures, H_2S being removed :

$$SC(NH_2)_2 = NC \cdot NH_2 + H_2S.$$

Like urea, it is a tautomeric substance and may react in either of two forms (E. A. Werner, *loc. cit.*) :



Urea and thiourea are used in large quantities in the manufacture of urea-formaldehyde resins (e.g. Beetle ware).

238. Uric acid, $C_5H_4N_4O_3$. Uric acid is a white crystalline powder, almost insoluble in cold water or alcohol, soluble in concentrated sulphuric acid and reprecipitated in water. It dissolves in alkalis, forming monometallic salts.

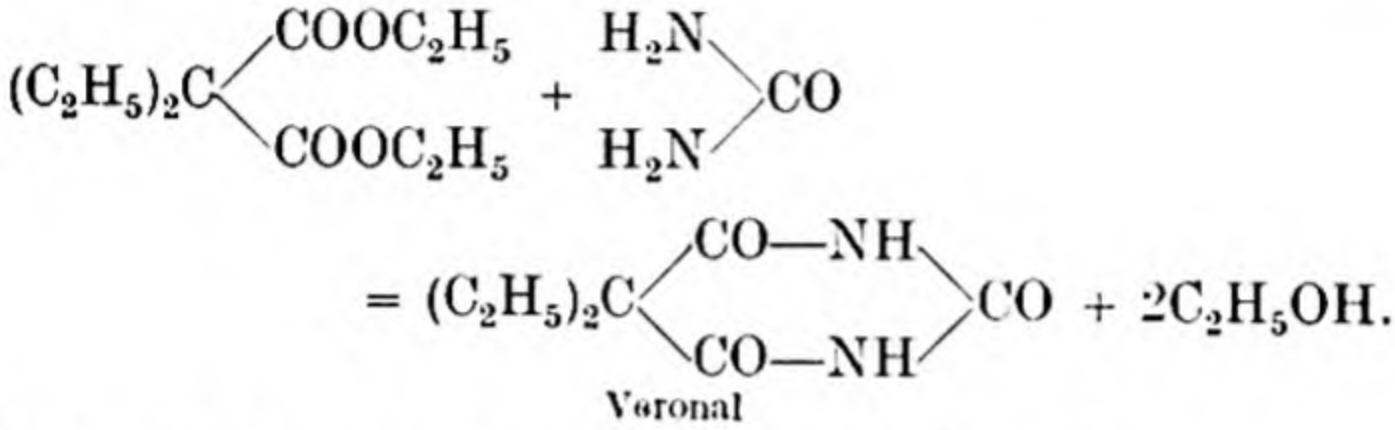
1. Heated alone, it decomposes into NH_3, HCN, urea, cyanuric acid, ammonium cyanate and carbonate, and some free carbon.

2. Moisten a little uric acid in a porcelain dish with conc. HNO_3 and dry carefully over the flame. A yellow or red residue

is obtained. When this (one half of it) is moistened with NH_4OH, an intense purple colour is produced—ammonium purpurate or murexide, $C_8H_4N_5O_6(NH_4)$. Caustic soda added to the other portion gives a blue colour.

3. A solution of sodium urate also reduces silver nitrate, Fehling's solution on prolonged boiling, and $KMnO_4$.

Veronal (C-diethylmalonyl urea) is an important derivative of urea, prepared by condensing urea with the ester of diethylmalonic acid in presence of sodium ethoxide :



Veronal

It belongs to the group of compounds called ureides, condensation products of urea with dibasic acids. It is an important hypnotic, much used in medicine.

239. Caffeine (1 : 3 : 7 . Trimethylxanthine),

$$C_5H(CH_3)_3N_4O_2 + H_2O.$$

Caffeine (theine) is closely related to uric acid. It is found in tea and coffee, and may be obtained from these (or from tea dust) by boiling with water, precipitating the tannic acid with lead acetate, removing the excess of lead from the filtrate with sulphuretted hydrogen, and concentrating the liquor. The crystalline deposit obtained on cooling is recrystallised.

It may also be made synthetically in several ways

Caffeine crystallises in white, glistening, silky needles, subliming about 178°, and melting at 236·8°. It is odourless, slightly soluble in water, and the solutions have a bitter taste.

It is used as a nerve stimulant, alone or in admixture with acetanilide, phenacetin, or as citrated caffeine.

REACTION. Evaporate a solution of a little caffeine in 1–2 c.c. hydrochloric acid, containing a small crystal of $KClO_3$, to dryness

in a small porcelain dish, and invert the dish over a clock-glass containing a few drops of ammonia solution. The residue acquires a deep purple colour, destroyed by caustic alkalis.

Theobromine (3 : 7-dimethylxanthine) is another natural product, closely related to caffeine, into which it may be converted by the action of methyl iodide on the potassium or silver salt. It is found in cocoa (1 to 2 per cent.) and is a crystalline powder, subliming unchanged about 290°. It is of some value as a diuretic.

AROMATIC COMPOUNDS

HYDROCARBONS

240. Benzene, C_6H_6, is obtained on the large scale by fractionating the light oil (80–170°) that distils from coal tar. Commercial benzene contains thiophene, C_4H_4S, which gives a blue colour when the benzene is shaken with sulphuric acid and a small crystal of isatin.

Pure benzene can be prepared by heating benzoic acid with lime or caustic soda (compare preparation of methane, 193) :

$$C_6H_5COONa + NaOH = Na_2CO_3 + C_6H_6.$$

It is a colourless mobile liquid, almost insoluble in water, but miscible with alcohol and ether. B.p. 80·5° ; m.p. 5·5° ; sp. gr. ·874 at 20°. It is very inflammable and burns with a luminous smoky flame. Benzene is a good solvent for fats, pitch, etc., and is used for dry cleaning.

REACTIONS. 1. Warm a little benzene with conc. sulphuric acid. The benzene gradually dissolves, forming benzenesulphonic acid :

$$C_6H_6 + H_2SO_4 = C_6H_5SO_3H + H_2O.$$

2. Add a little mixture of conc. nitric and sulphuric acids to benzene and shake vigorously, cooling if necessary. The liquid separates into two layers. The upper layer is nitrobenzene and has an agreeable smell recalling that of benzaldehyde :

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

3. Add 2 drops of bromine to 1 or 2 c.c. of benzene in a test-tube. There is no reaction in the cold, but on adding a bromine carrier such as a little iron powder or aluminium amalgam, substitution begins, with evolution of hydrogen bromide :

$$C_6H_6 + Br_2 = C_6H_5Br + HBr.$$

Warm slightly to complete the reaction, then throw into cold water. Bromobenzene separates as a heavy oil.

Toluene (Methylbenzene), $C_6H_5CH_3$. Toluene is obtained in the same distillation of the light oil from coal tar, but at a higher temperature. This is the only technical source of toluene, but it may be prepared synthetically in many ways. It is a colourless, refractive liquid of sp. gr. ·8841 at 0° and b.p. 110·7°.

Toluene is readily oxidised to benzoic acid, and may be detected by this means in benzene, which is much more stable. Boil the hydrocarbon in a reflux apparatus with an equal volume of saturated sodium dichromate solution and of sulphuric acid :

$$2C_6H_5CH_3 + 3O_2 = 2C_6H_5COOH + 2H_2O.$$

After an hour, pour the mixture into crushed ice, reduce unchanged dichromate with sulphurous acid, alkalize with solid sodium carbonate, shake well and separate from the benzene. Acidify the aqueous liquid with sulphuric acid, extract the liberated benzoic acid with ether, dry the ethereal extract with anhydrous sodium sulphate, and distil the ether. Sublime the residue from a porcelain dish, through dry filter-paper, to a clock-glass placed over it. Benzoic acid forms colourless needles of m.p. 122°. The reactions are given below (276).

Naphthalene, $C_{10}H_8$, is obtained from the carbolic oil fraction of coal tar (170–240°), of which it forms the greater portion. It crystallises from alcohol or ether in lustrous white plates of m.p. 80° and b.p. 218°. It is insoluble in water, sublimes readily and is volatile in steam. It is used as a preventive of moths, for the manufacture of phthalic acid, and its derivatives, the naphthols and naphthylamines, are of great importance in the manufacture of dyes.

Nitration yields α-nitronaphthalene, crystallising from alcohol or acetic acid in yellow needles of m.p. 61° and b.p. 304°.

Naphthalene picrate, $C_{10}H_8 . C_6H_2OH(NO_2)_3$, crystallises in golden yellow needles on mixing alcoholic solutions of the two substances. It melts at 149·5° and serves for the estimation of naphthalene.

Anthracene, $C_{14}H_{10}$, crystallises from the anthracene oil fraction of coal tar, boiling above 270°. The pure hydrocarbon crystallises in lustrous, fluorescent scales; m.p. 213°, b.p. 351°. It is insoluble in water, slightly soluble in alcohol and ether, easily soluble in hot benzene. Chromic acid or nitric acid oxidises it to anthraquinone, $C_{14}H_8O_2$, which crystallises in yellow needles or prisms melting at 285°, and anthracene is estimated in this way, or by means of the picrate, which forms red needles melting at 138°.

241. **Ethylbenzene**, $C_6H_5C_2H_5$, does not occur in coal tar. It may be prepared synthetically by the Friedel and Crafts reaction, from benzene and ethyl bromide in presence of aluminium chloride:

$$C_6H_6 + C_2H_5Br \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HBr,$$

or by Fittig's reaction in which metallic sodium acts on a mixture of two bromoderivatives.

$$C_6H_5Br + C_2H_5Br + 2Na \rightarrow C_6H_5C_2H_5 + 2NaBr.$$

100 c.c. of ether, free from water and alcohol (199), is placed in a dry half-litre flask, 24 g. of sodium wire quickly added and pushed under the ether, and the flask connected to an upright condenser. The flask is supported in an empty water-bath, to which cold water or crushed ice may be added if required. The mixture must stand until no trace of hydrogen escapes from the liquid, which may take some hours. Then a mixture of 50 g. bromobenzene with 40 g. ethyl bromide, carefully freed from alcohol, is added through the condenser, and the whole is allowed to stand overnight. If the ether shows a tendency to boil, cold

water or ice may be placed in the water-bath. Next day the metal has been corroded to a dirty powder. The ether is distilled from a water-bath, and the ethylbenzene then brought over by heating the flask with a large luminous flame, the burner being held in the hand. The residue in the flask consists of sodium bromide and excess of sodium, and the latter should be removed with alcohol before cleaning the flask.

The distillate should be redistilled using a short fractionating column. Ethylbenzene is a colourless refractive liquid of sp. gr. ·876 and b.p. 134°. Yield 18 g.

HALOGEN DERIVATIVES

Halogenated aromatic compounds may be obtained by (*a*) direct substitution by the halogen in the case of chlorine or bromine, (*b*) the action of phosphorus halides on alcohols or phenols, or (*c*) the Sandmeyer reaction (259) of diazonium salts. The second method is used only in special cases.

They are in general more stable than open-chain halogen derivatives, the halogen being much less readily replaced by OH, NH_2, CN and other groups. This stability, however, is greatly modified by the presence of other substituents in the ring, such as a NO_2 group in the position ortho or para to the halogen.

242. Chlorobenzene, C_6H_5Cl, is manufactured in large quantities by chlorination of benzene, at temperatures up to its boiling point, in presence of finely-divided iron or other catalyst. Further action yields chiefly *p*-dichlorobenzene.

In the laboratory it is much more convenient to prepare it by the Sandmeyer method (259) from aniline.

Chlorobenzene is a colourless, mobile, refractive oil of b.p. 132°, sp. gr. 1·11. It is insoluble in water, miscible with organic solvents.

It is used for the manufacture of aniline and of phenol by pressure reactions, and of nitrophenols and picric acid by hydrolysis of its nitration products.

243. Bromobenzene, C_6H_5Br. 50 g. of benzene are placed in the half-litre round-bottomed flask (Fig. 63) and 1 g. fine iron filings added, to act as a bromine carrier. The flask is placed in a basin of crushed ice to retard the reaction, which is at first vigorous. The upper flask (300 c.c.) contains about 150 c.c. of water, and is connected to the upper end of the condenser by a tube which must not enter the water, but end 1–2 cm. above it. The water absorbs the hydrogen bromide evolved during the reaction :

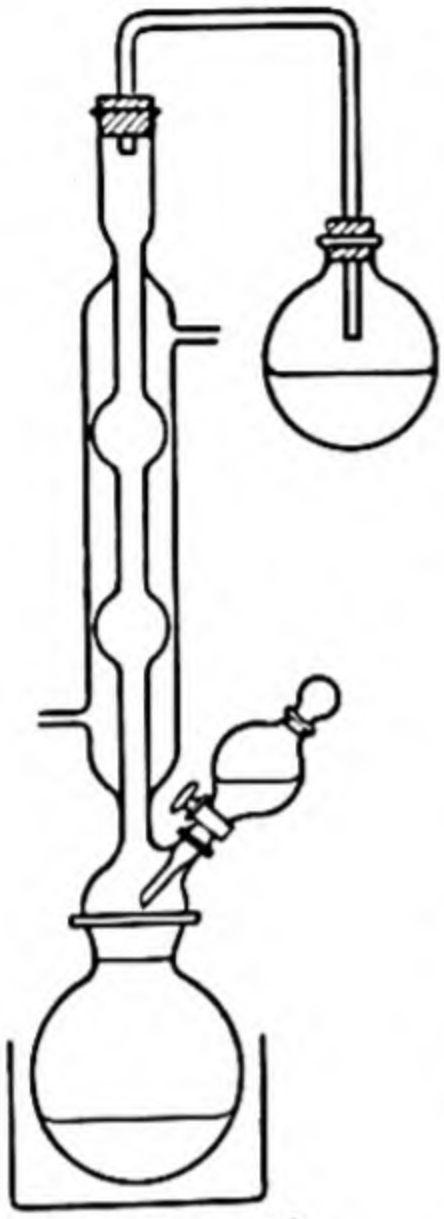


FIG. 63.

$$C_6H_6 + Br_2 = C_6H_5Br + HBr.$$

When the benzene is partly frozen, 35 c.c. (105 g.) of bromine is placed in the tap-funnel (50 c.c.), which is ground in to the widened end of the condenser-tube, the latter being itself ground to fit the neck of the flask. This avoids the use of cork or rubber in proximity to the bromine vapour. The bromine is allowed to enter the benzene, when the reaction at once sets in. If it is very slow, the ice water may be removed for a little. The reaction proceeds smoothly, becoming vigorous for a time. When it slackens, the ice is removed and replaced by hot water, and this continued until bromine vapour is no longer visible in the flask.

The contents of the flask are now transferred to a steam distillation apparatus, a slight excess of sodium hydroxide added, and the bromobenzene distilled in steam. When crystals begin to form in the condenser, the receiver is changed and the distillation completed. The bromobenzene is separated, washed with water, transferred to a small flask with dry calcium chloride, and next day filtered and distilled over a small naked flame, collecting separately the fraction 140–170°. This is redistilled, collecting at 150–160°.

Bromobenzene is a colourless highly refractive liquid of b.p. 157° and sp. gr. 1·50.

244. Dibromobenzene,

Paradibromobenzene is produced in small amounts in the above bromination. It is most effectively separated by steam distillation as described. The crystals formed in the condenser are dissolved in alcohol. Any crystals which appear in the cold residues from the distillations are dried on porous plate or filter paper, and also dissolved in alcohol. The mixed alcoholic solutions are carefully concentrated.

p-Dibromobenzene crystallises in colourless plates of m.p. 89·3° ; b.p. 219°.

Iodobenzene, C_6H_5I, is most easily prepared from benzene diazonium chloride by warming it with potassium iodide solution (258).

***p*-Chlorotoluene,** $CH_3C_6H_4Cl$, is also obtained in good yield from the diazonium salt (259).

NITRO COMPOUNDS

245. Nitrobenzene, $C_6H_5 . NO_2$. 50 g. of benzene are placed in a 400–500 c.c. flask, and a cold mixture of 100 g. nitric acid of sp. gr. 1·41 with 150 g. conc. sulphuric acid is slowly added, a few c.c. at a time, the benzene being vigorously shaken after each addition, and cooled if necessary. Copious red fumes are evolved, and the temperature should not be allowed to rise above 30° during the operation. When all the mixed acid has been added, the flask is heated to about 60° for half an hour, with frequent shaking. The nitrobenzene forms the upper layer.

When cold, the contents of the flask are transferred to a separating funnel, the spent acid run off, and the nitrobenzene washed with water, then with sodium carbonate solution, and again with water. The oil is then run off into a dry flask, some dry calcium chloride is added and the mixture allowed to stand overnight. The nitrobenzene should now be quite transparent, and is ready for distillation. This is done by decanting or filtering it into a

small distilling flask, which should not be more than half full, and fitting this to an air-condenser. Heat with a small flame close to the glass. A little water comes over first about 100°, and the temperature then rises rapidly to 200°. Collect between 200° and 212°.

Nitrobenzene is a colourless, strongly refractive liquid, smelling like bitter almonds. It is poisonous, insoluble in water, but miscible in any proportion with alcohol, ether or benzene. M.p. 6°; b.p. 211°; D^{15}_{4} 1·209. Yield 76–77 g.

246. *m*-Dinitrobenzene, $C_6H_4(NO_2)_2$. To 25 g. nitrobenzene in a 250 c.c. round flask is added gradually with vigorous shaking a mixture of 20 g. fuming HNO_3 and 30 g. H_2SO_4. The temperature should be 50–60°, and when all the acid has been added, the mixture is heated to 100° on a boiling water or steam bath, with frequent shaking, until in about one hour a drop of the oil solidifies on throwing into cold water. Allow the mixture to cool, pour on to crushed ice and collect the solid dinitrobenzene. Wash with water, melt in hot water and again cool and filter. Crystallise from alcohol. *m*-Dinitrobenzene separates in fine pale-yellow needles of m.p. 91°, b.p. 297°. Small quantities of the *o*- and *p*-dinitrobenzenes, melting at 118° and 172° respectively, remain dissolved. Yield about 30 g.

m-Dinitrobenzene is used for the manufacture of *m*-nitroaniline and *m*-phenylene diamine:

$$C_6H_4\langle^{NO_2}_{NO_2} \xrightarrow[H]{} C_6H_4\langle^{NH_2}_{NO_2} \xrightarrow[H]{} C_6H_4\langle^{NH_2}_{NH_2}.$$

247. Nitro-toluenes. Nitration of toluene produces mainly the ortho- and para-nitrotoluenes in the proportion of nearly three parts to two:

	ortho	*para*	*meta*
m.p. - -	α, −10·56°;	54·4°	16·0°
- -	β, −4·25°		
b.p. - -	225·7°	237·7°	231°
sp. gr. -	1·1742 (4°)	1·1392 (55°)	1·1600 (17·5°)
proportion -	57	40	3

The method is similar to that used for nitrobenzene. Take 50 g. toluene, and add gradually, with vigorous shaking, at 20–30°, a mixture of 40 g. fuming HNO_3 (coml. 95 per cent.) and 80 g. conc. H_2SO_4. When all the acid has been added, heat on the water-bath to 50–60° for an hour to ensure complete nitration, cool and allow to settle in a separator. Run off the acid, wash the oil with water and Na_2CO_3 solution, and dry. To separate the isomerides, use one of the following methods :

(*a*) Cool the oil in a porcelain or glass beaker, surrounded by a good mixture of crushed ice and salt. The para-compound crystallises. Prepare a filter meanwhile by cooling the Buchner funnel in ice water, dry it quickly and filter rapidly at the pump. The solid is recrystallised from alcohol and the oil is distilled as in method (*b*).

(*b*) The crude oil is distilled, using a short column, and preferably under reduced pressure. The first half of the distillate is mainly *o*-nitro-toluene. Stop the distillation at this point ; freeze the residue as in (*a*), and redistil the first distillate up to 227°, then add the residue to the freezing portion. Repeat the distillation and freezing, as far as practicable. Recrystallise the solid *p*-compound as in (*a*).

Note the yield of crude nitro-toluene and of each of the isomerides.

Further nitration of toluene yields 2 : 4-**dinitrotoluene** from either *o*- or *p*-nitrotoluene with more concentrated acid at 50°, and at 100° 2 : 4 : 6-**trinitrotoluene** is obtained. This is commonly known as T.N.T., and is manufactured for use as a high explosive. It melts at 81° and is quite safe in manufacture and handling. It is exploded by means of a detonator in the shell.

248. ***m*-Nitroaniline.** When aniline is nitrated as for benzene, much oxidation takes place with production of tar. At low temperatures, however, and in dilute sulphuric acid solution, a quantity of *m*-nitroaniline is obtained. It is better to reduce one of the groups in *m*-dinitrobenzene. This may be done in two ways.

(*a*) 10 g. *m*-dinitrobenzene is dissolved in 25 c.c. of alcohol,

10 c.c. conc. aqueous ammonia added, and the liquid after weighing saturated with H_2S. The flask is closed and set in a warm place until the smell of H_2S has disappeared. The liquid is cooled, again saturated, and the process repeated until the increase in weight is that required (5·5 g.). The product is precipitated by adding 150 c.c. water, filtered, dissolved in dilute HCl to free it from unchanged dinitrobenzene, again precipitated with ammonia, and crystallised from alcohol. Compare the yield with that obtained by the second method.

(*b*) A solution of sodium disulphide, Na_2S_2, is prepared by dissolving 37·5 g. cryst. Na_2S (or 12·5 g. anhydrous Na_2S) in 150–200 c.c. water, adding 10 g. flowers of sulphur and boiling. This solution is added gradually to a boiling mixture of 25 g. *m*-dinitrobenzene and 1 litre of water, which is well shaken and stirred to break up the molten dinitrobenzene. The mixture is kept boiling, and when the reduction is complete (all dissolved) the whole is filtered hot through a fluted or Buchner filter, the residue washed with a little hot water, and the filtrate set aside to cool. *m*-Nitroaniline crystallises from this liquor in yellow needles, m.p. 114°. Yield, 17 g. (88 per cent.).

AROMATIC AMINES

249. Aniline, $C_6H_5 . NH_2$, is manufactured by the reduction of nitrobenzene, and is so prepared in the laboratory :

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

On the large scale iron borings are used for the reduction, with a small quantity of hydrochloric acid ; the ferrous chloride acts as a carrier of oxygen, leaving black ferroso-ferric oxide, Fe_3O_4.

A similar method is used for the manufacture of the toluidines from ortho- and para-nitrotoluenes.

Aniline can also be manufactured from chlorobenzene by heating under pressure with ammonium chloride or aqueous ammonia at 200° ; a little Cu_2O or Cu_2Cl_2 is added : *

$$C_6H_5Cl + NH_4Cl = C_6H_5NH_2HCl + HCl.$$

* Frolich, *Indus. Engr. Chem.* **23,** 111 (1931).

The product is purer than that obtained from nitrobenzene, and the yield is 90 per cent. of the theoretical quantity.

In the laboratory nitrobenzene is reduced with tin and hydrochloric acid.

50 g. of nitrobenzene and 90 g. of granulated tin are placed in a round-bottomed litre flask. Conc. hydrochloric acid is added in small quantities, the mixture being well shaken after each addition, and kept cool by immersing the flask in cold water. A considerable amount of heat is generated, and it is advisable to attach a condenser tube to the mouth of the flask. About 300 c.c. of acid will be required, and the reaction is over when there is no further development of heat, and the smell of nitrobenzene has disappeared.

The acid liquid is now decanted from any undissolved tin, and made alkaline by adding a conc. solution of caustic soda until the precipitated tin hydroxide has just redissolved. The aniline is liberated from its salt, and may be extracted from the cold liquor with ether, or preferably distilled in a current of steam. The apparatus for this purpose is shown in Fig. 41. The aniline may be separated from the distillate in a separating funnel or by extraction with ether or chloroform. In the latter case the solution may be dried over anhydrous sodium sulphate for several hours, the solvent recovered by distilling from a water-bath, and the remaining aniline then distilled over a small flame.

Toluidines may be obtained similarly by reduction of the nitrotoluenes.

Aniline is a colourless, highly refractive liquid, soon turning yellow and brown on standing, especially in air. B.p. 184°, sp. gr. 1·026 at 15°. It is only slightly soluble in water, but dissolves readily in most organic solvents. It is a mon-acid base, most of the salts being easily soluble.

REACTIONS. 1. Mix a few drops of aniline on a watch-glass with an equal volume of conc. HCl. The hydrochloride,

$$C_6H_5NH_2 . HCl,$$

crystallises (aniline salt).

2. Dissolve a little of this in water, and add a few drops of

NaOCl or bleaching powder solution. An intense violet colour is produced.

3. To the last test add further a drop of ammonium sulphide. A rose-red colour is produced (detects 1 part aniline in 200,000 of water).

4. To a little aniline add conc. H_2SO_4 and a crystal of $K_2Cr_2O_7$; an intense blue colour is obtained.

5. Isonitrile reaction. Dissolve one or two drops of aniline and an equal volume of chloroform in 1–2 c.c. alcohol. Add a small piece of solid KOH or NaOH and warm. Phenyl isonitrile is produced and is recognised by its very disagreeable smell.

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5NC + 3KCl + 3H_2O.$$

6. Diazo-test. Dissolve a drop of aniline in dilute HCl, and add a little $NaNO_2$ solution. Divide into two parts. Boil one part; nitrogen is evolved, and the liquid smells of phenol:

$$C_6H_5N_2Cl + H_2O = C_6H_5OH + N_2 + HCl.$$

Pour the other part into a solution of β-naphthol in NaOH; a bright red ppt. is thrown down (phenylazo-β-naphthol).

7. To an aqueous solution of aniline or its salt add a little bromine water. White, crystalline 2 : 4 : 6-tribromoaniline is precipitated, melting at 119°:

$$C_6H_5NH_2 + 3Br_2 = C_6H_2Br_3NH_2 + 3HBr.$$

This reaction may be used for the estimation of aniline, as it is for phenol (463).

8. Mix 1-2 c.c. aniline with an equal volume of formalin and of water, shake well and heat on a water-bath. Anhydroformaldehydeaniline, $C_6H_5N : CH_2$, remains as a colourless solid.

250. Methyl aniline, $C_6H_5NHCH_3$. Methyl aniline may be obtained by hydrogenation of anhydroformaldehydeaniline:

$$C_6H_5 . N : CH_2 + 2H \rightarrow C_6H_5NHCH_3.$$

It is usually manufactured by heating a mixture of aniline and methyl alcohol with some hydrochloric acid under pressure in an autoclave:

$$C_6H_5 . NH_2 + CH_3OH + HCl = C_6H_5NHCH_3 . HCl + H_2O.$$

In the laboratory method methyl iodide is used. 25 g. aniline and 40 g. methyl iodide are placed in a flask and heated under a reflux condenser. A solution of 16 g. KOH in 50 c.c. methyl alcohol is added little by little so as to keep the liquid slightly alkaline, and the whole is boiled gently until, when practically all the KOH has been added, the liquid is permanently alkaline. On cooling, water is added to dissolve the potassium iodide, and the methyl aniline taken up in ether, which is separated, dried with sodium sulphate and evaporated. The residue is distilled.

Methyl aniline is a colourless, oily liquid of sp. gr. 0·976 and b.p. 193°. It is a stronger base than aniline. It gives no colour with bleaching powder solution. It does not give diazonium salts with nitrous acid, but the nitrosoamine, $C_6H_5N(NO)CH_3$. Heated to 300° with a little HCl, it passes mainly to *p*-toluidine.

251. Dimethylaniline, $C_6H_5N(CH_3)_2$. This is manufactured from aniline and methyl alcohol as for methyl aniline, but twice the amount of methyl alcohol is used, and a somewhat higher temperature and pressure.

$$C_6H_5NH_2 + 2CH_3OH + HCl = C_6H_5N(CH_3)_2HCl + 2H_2O.$$

Methyl aniline is used as the starting material in the laboratory method, in the same apparatus. 20 g. of methyl aniline with 27 g. methyl iodide are heated as before, and a solution of 12 g. KOH in 30 c.c. methyl alcohol added in small portions, keeping the mixture slightly alkaline. The preparation is completed as for methyl aniline.

Dimethylaniline is a colourless, refractive oil of sp. gr. ·958 and b.p. 193°. With nitrous acid it gives the *p*-nitroso-compound, $(CH_3)_2N \cdot C_6H_4NO$, which separates from HCl solution as the hydrochloride, in yellow needles sparingly soluble in water. From this the base is freed by shaking with a slight excess of NaOH solution, and extracted with ether, from which it crystallises in thin green flakes, m.p. 85°.

Dimethylaniline is largely used in the manufacture of dyes. The *para* position in the molecule is very sensitive to the action of substituents, and coupling with diazonium salts (257, 6), ketones (272, 1) and other compounds readily takes place.

Ethylaniline, b.p. 206°, and **diethylaniline**, b.p. 216°, are easily prepared from aniline and ethyl bromide, without the use of alkali in the boiling process. The mixture of aniline or ethylaniline and ethyl bromide in equivalent quantities is dissolved in twice its volume of alcohol, and as the boiling proceeds, the hydrobromide of the base crystallises out, rather suddenly in the case of diethylaniline.

$$C_6H_5NHC_2H_5 + C_2H_5Br = C_6H_5N(C_2H_5)_2HBr.$$

The alcohol is distilled from a water-bath, the residue cooled and decomposed with a slight excess of alkali, and the oily base separated in a funnel, dried with solid KOH and distilled.

252. Acetanilide (Antifebrin), $C_6H_5NHCOCH_3$. In a 500 c.c. flask place 25 g. of freshly distilled aniline and 150–200 c.c. water. Add in small quantities, with vigorous shaking, and in the cold, 30 g. acetic anhydride (colourless). Acetanilide is at once obtained in colourless plates :

$$C_6H_5NH_2 + (CH_3CO)_2O = C_6H_5NH \,.\, COCH_3 + CH_3COOH.$$

Filter and wash. The substance may be recrystallised from hot water, and melts at 114°. B.p. 304°.

Acetanilide is used in medicine as a febrifuge, and sold as *antifebrin*.

REACTIONS. 1. Boiled with caustic alkali or conc. HCl, it is hydrolysed into its constituents.

2. Isonitrile test. To a few mg. add 1–2 c.c. alcoholic NaOH and 1 c.c. $CHCl_3$ and warm gently. The nauseating odour of phenyl isonitrile is observed (**249**, 5).

Phenacetin, *p*-acetamino-ethoxybenzene,

$$C_2H_5OC_6H_4NHCOCH_3,$$

m.p. 135°, is somewhat similar to acetanilide in properties, but may be distinguished from it by the fact that a cold saturated solution gives no turbidity with bromine water. A red colour is produced on boiling with HCl and $FeCl_3$. Phenacetin also is used as an antipyretic and antineuralgic.

The acetyl group in these compounds not only diminishes or destroys the basic property of the substance, but renders the ring much less sensitive to the action of substituents. Bromine converts acetanilide into

p-**Bromoacetanilide,** $CH_3CONHC_6H_4Br$. Dissolve 5 g. acetanilide in 25 c.c. glacial acetic acid, and while keeping this solution cold, add gradually a solution of 6·5 g. bromine in 25 c.c. glacial acetic acid, shaking after each addition. Allow to stand in a warm place for half an hour, pour into cold water to precipitate the bromo-derivative and to remove the acids and slight excess of bromine, filter at the pump and wash with cold water. Crystallise from alcohol.

p-Bromoacetanilide crystallises in small colourless prisms, m.p. 167°. Yield 7–7·5 g. A small quantity of the ortho-compound is also formed, but remains dissolved in the alcohol.

p-**Nitroacetanilide,** $CH_3CONHC_6H_4NO_2$, is the chief product of nitration of acetanilide, a little of the ortho-nitro-compound also being formed.

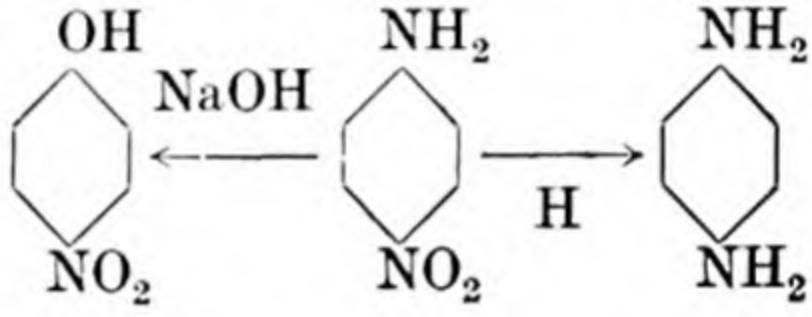
Place 15 g. acetanilide and 15 c.c. glacial acetic acid in a 100 c.c. beaker, and add carefully 25 c.c. conc. sulphuric acid, stirring until the acetanilide has dissolved. The mixture has become warm. Fix the beaker in a bowl of crushed ice and salt, and arrange a thermometer and a mechanical stirrer in the mixture. When the temperature has fallen below 5°, add drop by drop from a dropping funnel 6·5 c.c. of fuming HNO_3 (sp. gr. 1·5) so slowly that the temperature does not exceed 15°. The stirring must be continuous and efficient and should be continued for 10–15 minutes after all the acid has entered. Then remove the beaker from the ice and allow it to stand covered in a warm place for about an hour.

Pour the mixture into crushed ice, rinsing the beaker, thermometer and stirrer also with ice water. Break up and stir the yellow precipitate well, filter at the pump, wash well with cold water, and crystallise from alcohol. *p*-Nitroacetanilide forms colourless crystals, m.p. 212°. Yield 12–14 g.

p-**Nitroaniline,** $NH_2C_6H_4NO_2$, is obtained by hydrolysis of the acetyl derivative. Boil 10 g. of the last product in 45 c.c. of 70

per cent. H_2SO_4 under reflux for about an hour, pour the mixture into crushed ice and add NaOH solution in slight excess to precipitate the yellow *p*-nitroaniline. Filter at the pump and wash well with cold water. Recrystallise from hot alcohol, to which add half its volume of hot water before allowing to cool.

p-Nitroaniline crystallises in bright yellow needles or plates, m.p. 148°. It is a feeble base, its salts being decomposed by water. It yields a colourless diazonium salt, which couples with phenols and tertiary aromatic bases to yield important azo-dyes. When boiled with NaOH solution, *p*-nitroaniline yields *p*-nitrophenol, and when reduced, it forms *p*-phenylene-diamine.



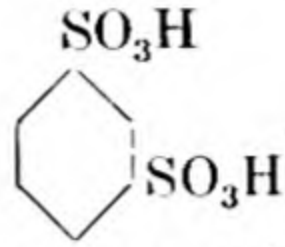
SULPHONIC ACIDS

253. Benzene sulphonic acid, $C_6H_5 . SO_3H$, is prepared by boiling under a reflux condenser a mixture of 50 g. of benzene and 300 g. conc. sulphuric acid, until the benzene is completely dissolved. The liquid is allowed to cool, poured on to some crushed ice and neutralised with chalk or milk of lime (" liming-out "). This forms the soluble calcium salt and calcium sulphate. The latter is removed by filtration, boiled with water and again filtered, and the combined filtrates evaporated.

Benzene sulphonic acid may be obtained free by mixing a solution of the calcium or barium salt with the equivalent amount of sulphuric acid. It crystallises in colourless deliquescent plates, very soluble in water and in alcohol. The anhydrous acid melts at 66°.

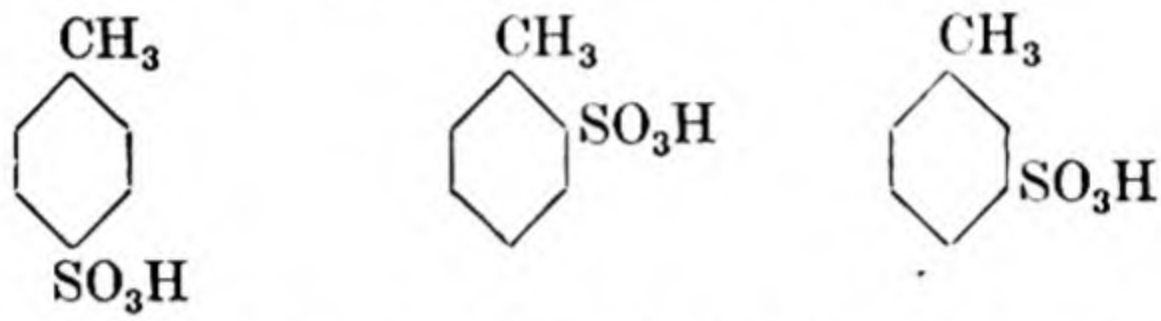
The salts are all soluble. The barium salt, $(C_6H_5SO_3)_2Ba . H_2O$, forms pearly leaflets. Alkali salts are obtained by the action of alkali carbonates on solutions of the Ca, Ba or Pb salts. The sodium salt is used in the manufacture of phenol by fusion with alkali :

$$C_6H_5SO_3Na + NaOH \rightarrow \underset{\text{Sodium phenate}}{C_6H_5ONa} + NaHSO_3.$$

254. Benzene disulphonic acid, 

. The *m*-compound is the chief product of heating benzene with fuming sulphuric acid at 200°, a little of the *p*-acid also being obtained. It is used for the manufacture of resorcinol, $C_6H_4(OH)_2$, *m*-dihydroxybenzene, just as phenol is obtained from sodium benzene sulphonate.

255. Toluene sulphonic acids. When toluene is sulphonated as described for benzene, the chief product is the para-sulphonic acid, with some ortho- and a little meta-acid.

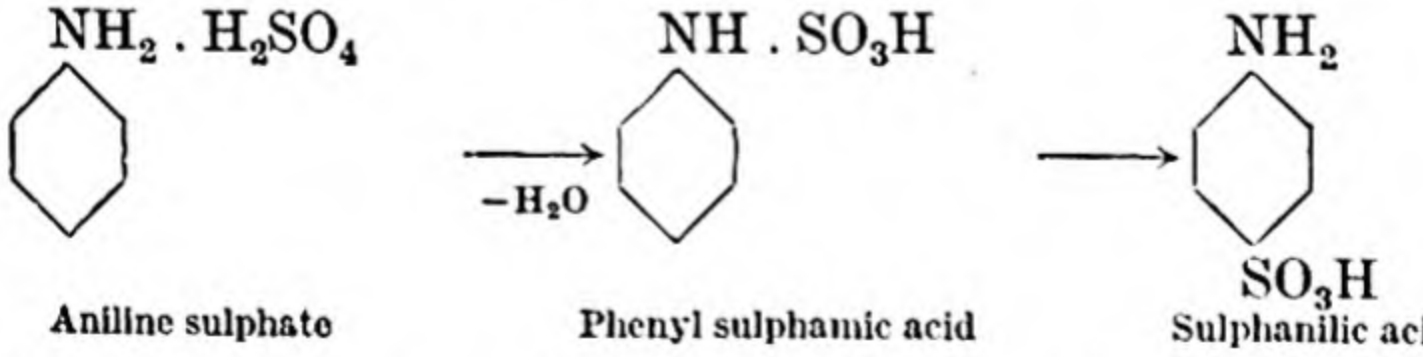


The methyl group may be oxidised with chromic acid mixture, with formation of the corresponding *sulphobenzoic* acids.

Alkali fusion forms the cresols, and to some extent, by oxidation of the methyl group, the hydroxybenzoic acids.

256. Sulphanilic acid, $NH_2C_6H_4SO_3H$, is aniline-*p*-sulphonic acid, and is of great industrial importance.

25 g. aniline is placed in a round short-necked flask and mixed carefully with 30 g. sulphuric acid. The sulphate is at first solid, but melts on heating the flask in an oil bath to 190–200°. The heating is continued for 6–8 hours.



Aniline sulphate — Phenyl sulphamic acid — Sulphanilic acid

On cooling, the grey mass is dissolved in hot water, filtered and evaporated. Sulphanilic acid crystallises in colourless rhombic plates with 1 mol. H_2O, which effloresce in dry air. It is only

slightly soluble in cold water (1 in 112 at 15°). On fusing with alkali, the SO_3H group is not replaced by OH, but aniline is regenerated. Oxidation in dilute H_2SO_4 solution converts it into quinone, $C_6H_4O_2$.

The acid does not melt, but decomposes on heating. It is largely used in the manufacture of azo-dyes.

DIAZONIUM SALTS

When a solution of aniline hydrochloride is mixed with nitrous acid, the diazonium salt is obtained :

$$C_6H_5NH_2 \,.\, HCl + HNO_2 \rightarrow \underset{\text{Phenyl diazonium chloride}}{[C_6H_5N \,\vdots\, N]^{\cdot}Cl'} + 2H_2O.$$

The free base and its salts are strongly ionised, and are converted by alkali into a tautomeric form :

$$[C_6H_5N \,\vdots\, N]^{\cdot}OH' \rightarrow \underset{\text{Benzene diazohydroxide}}{C_6H_5N : N \,.\, OH}.$$

The latter gives alkali salts, and reacts with phenols and tertiary amines to form azo dyes.

Diazonium salts are very reactive and unstable, and the temperature must be kept below 5°, sometimes lower.

257. Phenyldiazonium chloride. In a 500 c.c. flask or beaker dissolve 12 g. aniline in a mixture of 25 c.c. conc. HCl and 50 c.c. water. Cool well by surrounding the vessel with crushed ice in a bowl, adding a little ice also to the liquid. When the temperature has fallen to 5–0°, add slowly, with constant stirring, a solution of 9 g. $NaNO_2$ in 25 c.c. water, prepared just before use in order to utilise the cooling effect on dissolving the nitrite. The temperature must be kept below 5°. For large quantities the stirring may be arranged mechanically, as it is on the large scale, and the nitrite solution added through a dropping funnel. Towards the end, a drop of the liquid on a glass rod is tested with starch-iodide paper. An intense blue stain indicates free HNO_2. The diazotisation proceeds more slowly towards the end, and the test must be repeated, and nitrite added as required, until a *slight* permanent excess of nitrite remains.

Add ice water to make the volume 240 c.c. and remove 40 c.c. for the reactions. To the 200 c.c. add a solution of 3 g. urea in a little water, to decompose free nitrous acid, and allow to stand in the ice bath for iodobenzene while the reactions are studied.

REACTIONS. 1. To 5 c.c. of the diazo solution add a little more acid and boil. Nitrogen is evolved and phenol is produced :

$$C_6H_5N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl.$$

The reaction between solid diazonium salts and absolute methyl or ethyl alcohol forms the ether to the extent of 70 per cent., and a little of the hydrocarbon :

$$C_6H_5N_2Cl + C_2H_5OH \rightarrow \underset{\text{Phenetole, b.p. } 172^\circ.}{C_6H_5OC_2H_5} + N_2 + HCl.$$

$$C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

2. Replacement of the diazo group by hydrogen occurs on boiling with a solution of alkali stannite (310, 3) :

$$C_6H_5N_2Cl + K_2SnO_2 + KOH = C_6H_6 + N_2 + K_2SnO_3 + KCl.$$

3. Add 5 c.c. to a little KI solution : iodobenzene is formed, coloured with free iodine :

$$C_6H_5N_2Cl + KI = C_6H_5I + N_2 + KCl.$$

4. Mix 5 c.c. with a solution of 1 g. cuprous chloride in a little conc. HCl. Chlorobenzene separates on warming (Sandmeyer reaction) :

$$C_6H_5N_2Cl + Cu_2Cl_2 = C_6H_5N_2Cl \,.\, Cu_2Cl_2.$$

$$C_6H_5N_2Cl \,.\, Cu_2Cl_2 \xrightarrow[\text{Heat}]{} C_6H_5Cl + N_2 + Cu_2Cl_2.$$

A similar reaction occurs with cuprous bromide or cyanide.

5. To 5 c.c. add 1–2 c.c. aniline and shake. A yellow ppt. of diazoaminobenzene is formed (aniline yellow). This may appear in diazotising if the amount of acid be insufficient, but decomposes on addition of more acid :

$$C_6H_5N_2Cl + H_2NC_6H_5 \rightleftharpoons C_6H_5N : N \,.\, NHC_6H_5 + HCl.$$

6. Azo compounds are formed by coupling with phenols or tertiary bases, usually in presence of alkali. Add a few c.c. in

each case to alkaline solutions of phenol, of β-naphthol, and to a little dimethylaniline. Precipitates are formed respectively of *p*-hydroxyazobenzene, $C_6H_5N:N.C_6H_4OH$ (brown); *a*-phenylazo-β-naphthol, $C_6H_5N:N.C_{10}H_6OH$ (bright red), and *p*-dimethylamino-azobenzene, $C_6H_5N:N.C_6H_4N(CH_3)_2$ (butter-yellow).

258. Iodobenzene, C_6H_5I, is obtained by the direct replacement of the diazo group by iodine, by the action of potassium iodide. The latter is decomposed by nitrous acid, liberating iodine, and it is in order to minimise this action that urea is added to the diazonium solution **(236, 4)**:

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

Free nitrous acid is thus removed. To the 200 c.c. of diazo solution, equivalent to 10 g. aniline, is now added a solution of 20 g. KI in 50 c.c. water. The mixture is well stirred and allowed to stand in a warm place for some hours. It is then heated on a water-bath to complete the reaction. Iodobenzene separates as a heavy oil. On cooling it is extracted with ether or dichloroethylene, the extract separated, washed with NaOH solution and then with water, and dried over calcium chloride. The following day the liquid is decanted, the $CaCl_2$ washed with more solvent, the solvent recovered by distillation and the remaining oil fractionated.

Iodobenzene is a colourless, refractive liquid, b.p. 188°, sp. gr. 1·83. Yield about 15 g.

Iodobenzene dichloride, $C_6H_5ICl_2$, separates in yellow needles from a chloroform solution of iodobenzene into which dry chlorine is passed.

Iodosobenzene, $C_6H_5I:O$, is obtained by grinding the dichloride in a mortar with sodium hydroxide solution:

$$C_6H_5ICl_2 + 2NaOH = C_6H_5I:O + 2NaCl + H_2O.$$

This acts as a diacid base, forming a diacetate and other salts. It oxidises in air at 90–100°, or in hypochlorite solution, or by distilling in steam, into

$$2C_6H_5I:O \rightarrow C_6H_5IO_2 + C_6H_5I.$$

Iodoxybenzene, $C_6H_5IO_2$. This crystallises in white needles, explodes at 230°, and acts as an oxidising agent.

259. *p*-Chlorotoluene, $CH_3 . C_6H_4Cl$ (Sandmeyer's reaction). 20 g. *p*-toluidine, dissolved in a mixture of 50 c.c. conc. HCl and 50 c.c. water, is cooled by addition of 40–50 g. of crushed ice, the vessel also being surrounded by ice. When the temperature falls below 5°, the solution is diazotised by the slow addition of a solution of 14 g. $NaNO_2$ in 50 c.c. water. *p*-Tolyldiazonium chloride is produced. The same precautions must be taken as in the diazotisation of aniline, in regard to cooling and avoidance of an excess of nitrite.

Prepare a solution of 5–6 g. cuprous chloride in 100 c.c. conc. HCl, which need not be cooled, and pour the diazotised solution into this, mixing well. A brown addition compound, a covalent co-ordination cuprous diazonium salt, is formed, which decomposes slowly, more rapidly on warming, liberating nitrogen :

$$CH_3C_6H_4N_2Cl . Cu_2Cl_2 \rightarrow CH_3C_6H_4Cl + N_2 + Cu_2Cl_2.$$

The cuprous chloride is set free, and for this reason the amount required is much less than a molecular proportion. In Gattermann's modification of the Sandmeyer reaction a suspension of copper powder in concentrated HCl or other acid is used.

When the evolution of nitrogen has ceased, the mixture is distilled with steam and the colourless oil (more or less yellow with azo compound) is recovered and purified as described for iodobenzene.

p-Chlorotoluene is a colourless, mobile oil, b.p. 162·3°, sp. gr. 1·0847, insoluble in water, miscible with organic solvents. Yield, 18–20 g.

260. Diazoaminobenzene, $C_6H_5N : N . NH . C_6H_5$. Diazotise 10 g. of aniline as already described (257), carefully avoiding excess of nitrite. Dissolve another 10 g. aniline in the theoretical amount of HCl, cool the solution in ice water, and add it slowly with good stirring to the diazonium salt. Diazoaminobenzene is precipitated in golden yellow plates. The reaction is completed

by addition of a cold concentrated solution of 30 g. sodium acetate, and after standing for ½–1 hour the precipitate is filtered at the pump, washed with cold water and dried on a plate or paper. Yield, about 21 g.

$$C_6H_5N : N . OH + H_2NC_6H_5 \rightarrow C_6H_5N : N . NHC_6H_5 + H_2O.$$

261. Aminoazobenzene, $C_6H_5N : N\langle\bigcirc\rangle NH_2$. The isomeric change of diazoamino into aminoazo compounds is effected by warming with the free base or with acids in presence of the salt. It occurs slowly on standing in alcoholic solution.

10 g. finely powdered diazoaminobenzene and 5 g. aniline hydrochloride, also powdered, are placed in a small beaker with 25 g. pure aniline, and heated to 40–50° with frequent stirring for about an hour. The mixture is then poured into water in a large beaker and the aniline dissolved by adding acetic acid. The solid residue of aminoazobenzene is filtered, washed with water, and extracted in a large dish with successive quantities of HCl. From the acid solution aminoazobenzene hydrochloride crystallises in small dark-coloured prisms with a blue reflex. Yield 8–9 g.

262. Phenylhydrazine, $C_6H_5NH . NH_2$, is obtained by the reduction of diazobenzene salts, either with a solution of alkali bisulphite or with $SnCl_2$ in concentrated HCl.

Prepare a solution of the diazonium salt as before from 10 g. aniline, but keep the solution more concentrated by using only half the quantity of water ; add no ice to the liquid, but cool in an ice and salt bath.

Dissolve 45 g. $SnCl_2$ in 400 c.c. conc. HCl, cool this solution also below 0°, and pour it carefully into the diazonium solution, stirring well to ensure complete mixing. A double salt of phenylhydrazine with tin chloride separates, and is filtered at the pump and washed with very little cold water.

$$[C_6H_5N : N]'Cl' + 4H \rightarrow [C_6H_5NHNH_2]HCl.$$

The double salt may be used for the reactions. The free base

may be obtained by mixing the double salt with slight excess of NaOH, cooling well and extracting with ether.

Phenylhydrazine is a nearly colourless liquid, freezing at low temperatures to a crystalline mass melting at 19·6°, b.p. 243°. It is usually employed in the form of salts, such as the hydrochloride or acetate.

REACTIONS. 1. It is used as a reagent for aldehydes, ketones and similar compounds, with which it gives hydrazones :

$$(CH_3)_2CO + H_2N \cdot NHC_6H_5 = (CH_3)_2C : N \cdot NHC_6H_5 + H_2O.$$

With many of the sugars it first yields a hydrazone, which is then changed by a second reaction, involving oxidation of the adjacent group, into an osazone (see glucose, **230,** 6).

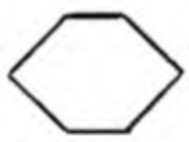
2. Phenylhydrazine reduces Fehling's solution, giving a red precipitate of cuprous oxide. Free nitrogen is liberated, and the hydrocarbon obtained :

$$C_6H_5NH \cdot NH_2 + 2CuO = Cu_2O + C_6H_6 + N_2 + H_2O.$$

3. Reduced with zinc dust and HCl, it is converted into aniline and ammonia :

$$C_6H_5NH \cdot NH_2 + 2H \rightarrow C_6H_5NH_2 + NH_3.$$

Phenylhydrazine is used in large quantities in the manufacture of *antipyrine.*

263. Helianthin, $(CH_3)_2N$  $N : N$ SO_3H, is an example of an azo-colour, prepared from dimethylaniline and diazotised sulphanilic acid. This acid is sparingly soluble in water and is diazotised by first preparing the sodium salt.

12 g. anhydrous sulphanilic acid is dissolved in a solution of 4 g. NaOH in 150 c.c. water. To this is added a solution of 5 g. $NaNO_2$ in 20 c.c. water, and when the mixture has been cooled to 0° in ice or ice and salt, it is diazotised by adding slowly, with constant stirring and an occasional test for free HNO_2, a mixture of 7·5 c.c. conc. HCl and 10 c.c. ice water. Excess of nitrous acid should be avoided.

9 g. dimethylaniline is dissolved in just sufficient dilute HCl (equal parts of conc. HCl and water), and the solution of di-

methylaniline hydrochloride added to the diazotised sulphanilic acid, well mixed and made slightly alkaline with sodium hydroxide. The sodium salt of helianthin is precipitated. The precipitation is made more complete by stirring in 30 g. common salt until dissolved, and allowing the mixture to stand for ½–1 hour. The ppt. is then filtered, washed with a little cold water, and recrystallised from hot water.

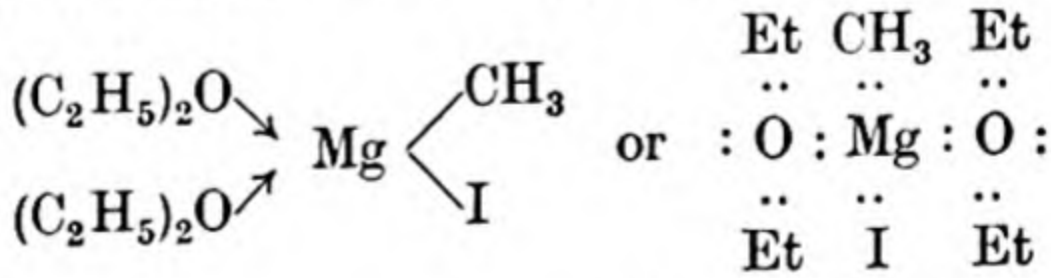
Methyl orange. The sodium salt of helianthin is used as an indicator under this name. It crystallises in small golden yellow plates. The solution dyes wool and silk yellow, but the colour is too easily changed to be of much use as a dye. Acids turn it red.

Helianthin hydrochloride, $SO_3H \cdot C_6H_4N : NC_6H_4N(CH_3)_2HCl$, crystallises in glistening violet plates when half the mother liquor from the recrystallised sodium salt is acidified with conc. HCl and evaporated.

Helianthin base, $SO_3HC_6H_4N : NC_6H_4N(CH_3)_2$, is obtained by acidifying the other half of the liquor with acetic acid.

THE GRIGNARD REACTION

264. Metallic magnesium reacts slowly with alkyl or aryl halogen derivatives, forming addition compounds of the type $CH_3 \cdot Mg \cdot I$. These were first examined in detail by Grignard,* and are usually called Grignard reagents. He found that in presence of anhydrous ether the reaction is much more vigorous, and the metal dissolves forming a clear colourless liquid. When the ether is distilled off, the magnesium compound remains as a colourless solid, which may contain combined ether in the form of a co-ordination complex which may be represented as:



These compounds are comparatively stable, the ether being retained at temperatures over 100°, and they react just as the simple compounds do. They may be obtained also by the

* *Comptes rendus* (1900), **130**, 1322.

aid of other solvents, as benzene containing a little ether, or a little of a tertiary base, or in dimethylaniline solution. The essential thing is that all the materials, as well as the vessels employed, should be perfectly dry.

The Grignard compounds are very reactive, and are of great value as synthetic agents. Hydrocarbons, alcohols of all classes, aldehydes, ketones, acids, and other types of compounds, may be obtained by the action of Grignard reagents on suitable substances. In the action of alkyl halides on magnesium, in addition to the magnesium alkyl halide, saturated hydrocarbons * are formed, in small quantity only among the lower homologues, but forming the chief product among the higher homologues.

$$1.\ CH_3I + Mg = Mg\begin{<}CH_3\\I\end{>}$$

$$2.\ 2C_nH_{2n+1}\,.\,X + Mg = MgX_2 + (C_nH_{2n+1})_2,$$

where X is a halogen atom.

The reagents are prepared just before use, owing to the difficulty of preserving them. They are at once decomposed by water, and moisture must be excluded from the atmosphere by placing a calcium chloride tube at the top of the reflux condenser during the preparation.

Reduction products † of the original materials (CH_3CHO, CH_3COCl, etc.), as well as of the synthetic compounds desired, are obtained as by-products in the Grignard reactions.

265. Ethyl magnesium iodide. Some thin magnesium ribbon is well cleaned with fine emery cloth, and broken into pieces 1–2 cm. long. Exactly 2·4 g. of this are placed in a small dish and heated in the air-bath at 110–120° for an hour to ensure dryness. It is then placed in a 250 c.c. round flask fitted with a reflux condenser, and mixed with a solution of 15·7 g. ethyl iodide in 50 c.c. of absolute ether. These materials must be previously dried, the ethyl iodide by being allowed to stand over

* Tissier and Grignard, *ibid.* (1901), **132,** 835.

† Whitmore and others, *J. Amer. Chem. Soc.* **60,** 2458 (1938).

calcium chloride all night and then redistilled, and the ether as described in par. **199.** A small crystal of iodine may be added to start the reaction, and the flask may be heated in a water-bath at first. When the reaction begins, much heat is developed, and the water-bath is removed, or cooled, the ether being kept gently boiling until, in about two hours, nearly all the magnesium has dissolved. The solution now contains ethyl magnesium iodide, $C_2H_5 . Mg . I$, and must be carefully protected from moisture.

266. Propionic acid, C_2H_5COOH. When the metal has all dissolved, remove the condenser and pass dry carbon dioxide slowly through the solution, which must be kept cool. An unstable addition compound of the composition $C_2H_5CO_2MgI$ is formed. This is decomposed by mixing with a little dilute H_2SO_4 and ice :

$$2C_2H_5CO_2MgI + H_2SO_4 = 2C_2H_5COOH + MgSO_4 + MgI_2.$$

Salt out the propionic acid by saturating the liquid with common salt. It separates as an oil, resembling acetic acid, b.p. 141°. The yield is over 50 per cent.

267. Benzoic acid from iodobenzene.* Prepare a quantity of phenyl magnesium iodide as just described, using 20·4 g. of iodobenzene in place of the ethyl iodide, and as soon as the magnesium has dissolved pass a slow stream of dry carbon dioxide for 2–3 hours, keeping the flask cool during this operation. The mixture separates into two layers, an upper layer of ether, and a heavy oily layer containing the complex magnesium compound, $C_6H_5 . CO . O . MgI$. This separation, however, may not occur if the temperature has been too high. In either case, the contents of the flask are now mixed with a little crushed ice, and treated with a cold mixture of 15 c.c. conc. hydrochloric acid and an equal volume of water. Benzoic acid is liberated :

$$2C_6H_5 . CO . OMgI \xrightarrow[\text{Water}]{} (C_6H_5COO)_2Mg + MgI_2.$$

$$(C_6H_5COO)_2Mg + 2HCl = 2C_6H_5 . COOH + MgCl_2.$$

* Zelinsky, *Ber.* (1902), **35,** 2692.

The benzoic acid is extracted with ether, the ether evaporated, and the residue purified by dissolving in sodium or potassium hydroxide, filtering from any undissolved substance, and again precipitating with hydrochloric acid. The yield of the crude acid is 10–12 g. Bromobenzene gives a much smaller yield.

268. **Phenylacetic acid,** $C_6H_5 . CH_2 . COOH$, may be prepared in a similar manner from benzyl chloride, using 12·7 g. of the freshly distilled substance in place of the iodobenzene in the previous experiment. When dry carbon dioxide is passed through the ethereal solution of benzyl magnesium chloride, colourless crystals of the composition, $C_6H_5 . CH_2 . CO . OMgCl . (C_2H_5)_2O$, are obtained. This is treated in the same manner as the reaction product already described. Yield about 10 g.

Phenylacetic acid forms colourless glistening leaflets melting at 76°, and boils without decomposition at 265·5°. It is sparingly soluble in cold water, more readily on heating.

269. *tert*-**Butyl alcohol.** The Grignard reagents yield primary alcohols on treatment with formaldehyde in the polymeric form of trioxymethylene. Other aldehydes yield secondary alcohols, and ketones give tertiary alcohols.

Prepare methyl magnesium iodide by the method described above, using 14·2 g. CH_3I, the other quantities being as before. When the metal has dissolved, add a solution of 6 g. pure dry acetone in 30 c.c. ether. The addition compound separates in crystalline form :

$$CH_3MgI + (CH_3)_2CO \rightarrow (CH_3)_3C . OMgI . (C_2H_5)_2O.$$

This is decomposed by addition of a little ice-cold dilute H_2SO_4, the ethereal solution separated and the aqueous solution extracted twice with a little ether. The whole ethereal extract is set aside to dry overnight with anhydrous Na_2SO_4, the ether evaporated and the butyl alcohol, $(CH_3)_3COH$, distilled. It is a colourless liquid, sparingly soluble in water, f.p. 25·5°, b.p. 83°, sp. gr. ·786. Yield, 4–5 g.

270. Benzhydrol, $(C_6H_5)_2CH \cdot OH$, may be taken as an example of the synthesis of a secondary alcohol. It is obtained by the condensation of phenyl magnesium iodide with benzaldehyde, the product being then decomposed with dilute hydrochloric acid :

$$C_6H_5 \cdot CHO + C_6H_5 \cdot Mg \cdot I = (C_6H_5)_2CH \cdot O \cdot MgI.$$

$$(C_6H_5)_2CH \cdot OMgI + HCl = (C_6H_5)_2 \cdot CH \cdot OH + Mg(I)Cl.$$

A solution of phenyl magnesium iodide, prepared as already described, is slowly added to a solution of 10·6 g. of freshly distilled benzaldehyde in 30 c.c. of absolute ether. The mixture should be well shaken, and the flask cooled in ice water. A vigorous reaction occurs, and the intermediate compound above separates as a yellowish white precipitate. When all the Grignard compound has been added, the reaction is completed by heating on the water-bath for half an hour. The mixture is then treated with crushed ice and acid, and placed in a separating funnel, from which the aqueous layer is run off and extracted twice with 25 c.c. of ordinary ether. The extract is added to the original ethereal solution, and the whole is shaken with a dilute solution of sodium bisulphite to remove unchanged benzaldehyde. It is then dried with anhydrous sodium sulphate, and the ether distilled. An oily residue is obtained, which solidifies on cooling. The crystals are dried on a porous plate and recrystallised from ligroin. Yield, 12–13 g.

Benzhydrol forms colourless needles, melting at 68°.

In a similar manner the tertiary alcohol, triphenylcarbinol, may be obtained from the ketone benzophenone.

271. Benzyl alcohol, $C_6H_5CH_2OH$. The hydrogen in benzene and its homologues can be directly replaced by chlorine. Toluene in presence of a polar catalyst is chlorinated in the nucleus, yielding *o*- and *p*-chlorotoluenes; at the boiling point, on the other hand, or in sunlight, benzyl chloride, $C_6H_5CH_2Cl$, benzal chloride, $C_6H_5CHCl_2$, and benzotrichloride, $C_6H_5CCl_3$, are successively produced.

When benzyl chloride is boiled with a solution of potassium

carbonate, benzyl alcohol is produced and can be obtained from the cold mixture by extraction with ether :

$$2C_6H_5CH_2Cl + K_2CO_3 + H_2O = 2C_6H_5CH_2OH + 2KCl + CO_2.$$

The higher chlorination products correspond similarly with benzaldehyde and benzoic acid :

$$\begin{array}{ccccccc} C_6H_5 . CH_3 & \rightarrow & C_6H_5 . CH_2Cl & \rightarrow & C_6H_5 . CHCl_2 & \rightarrow & C_6H_5 . CCl_3. \\ & & \downarrow & & \downarrow & & \downarrow \\ & & C_6H_5 . CH_2OH & \rightarrow & C_6H_5 . CHO & \rightarrow & C_6H_5 . COOH. \end{array}$$

Benzyl alcohol is a colourless liquid with a faint aromatic smell, and boils at 206°. It is soluble in water, miscible with organic solvents. In its properties it resembles the aliphatic alcohols, and differs widely from the isomeric cresols.

Reactions. 1. Warm a little of the alcohol with conc. hydrochloric acid. Drops of benzyl chloride form and slowly rise to the surface.

2. Add conc. nitric acid carefully to a few drops of benzyl alcohol. Oxidation occurs, and on neutralising the nitric acid, the characteristic smell of benzaldehyde is observed.

272. Benzaldehyde, $C_6H_5 . CHO$. When benzal chloride is boiled with a solution of potassium carbonate, benzaldehyde is produced :

$$C_6H_5CHCl_2 \rightarrow [C_6H_5 . CH(OH)_2] \rightarrow C_6H_5 . CHO.$$

Benzaldehyde is a colourless liquid with a smell like that of bitter almonds ; b.p. 179°, sp. gr. 1·05. It oxidises rapidly on exposure to air, forming benzoic acid. It has many properties in common with the aliphatic aldehydes, but does not reduce Fehling's solution. It differs also in the products obtained when treated with caustic alkalis, ammonia and potassium cyanide.

Reactions. 1. A few drops of benzaldehyde and an equal volume of dimethylaniline are warmed in a test-tube with a pellet of $ZnCl_2$. An intense green colour is developed (malachite green).

2. 1 c.c. each of aniline and benzaldehyde are mixed in a test-tube. Heat is developed, and benzylidene-aniline is formed ($C_6H_5CH : NC_6H_5$). On cooling this separates in colourless prisms, m.p. 45°.

In order to obtain benzaldehyde free from benzoic acid for the following experiments, about 150–200 c.c. should be distilled, using an air condenser. Collect the benzaldehyde at 178–180°.

273. **Benzyl alcohol and Benzoic acid,** from Benzaldehyde (Cannizzaro's reaction). 20 g. benzaldehyde and a cold solution of 25 g. KOH in 30 c.c. water are shaken together in a separator and the emulsion allowed to stand, with frequent shaking, for 1–2 hours.

$$2C_6H_5CHO + KOH \rightarrow C_6H_5CH_2OH + C_6H_5COOK.$$

On cooling, the alcohol is extracted with ether, the extract dried overnight, the ether evaporated, and the alcohol distilled.

The benzoic acid is pptd. from the aqueous solution by acidifying with HCl, filtered, washed with a little cold water and recrystallised from hot water.

274. **Benzoin,** $C_6H_5CHOH \cdot COC_6H_5$. Boil 10 g. of benzaldehyde in a round flask with a solution of 3 g. KCN in 75 c.c. alcohol, under a reflux condenser, adding a few chips of porous pot to prevent superheating. Two molecules of the aldehyde condense to form benzoin. After boiling for an hour, pour the liquid into a beaker or crystallising dish. On cooling, benzoin crystallises in colourless prisms, m.p. 137°. The mother liquor may be concentrated to obtain a second crop, and the whole recrystallised from fresh alcohol. Yield, 8–9 g.

275. **Benzil,** $C_6H_5CO \cdot COC_6H_5$. Place 5 g. of benzoin with 25 c.c. conc. HNO_3 in a covered beaker, and warm gently until no more red fumes are evolved. Dilute with water, filter and crystallise from alcohol. Benzil crystallises in yellow prisms, m.p. 93°.

276. **Benzoic acid,** C_6H_5COOH, is almost all produced by boiling benzotrichloride with milk of lime :

$$C_6H_5CCl_3 \rightarrow [C_6H_5C(OH)_3] \rightarrow C_6H_5COOH.$$

Some is made by oxidising benzyl chloride, $C_6H_5CH_2Cl$, with dilute nitric acid, and also by the vapour phase oxidation of toluene in presence of certain metallic oxides.

For pharmaceutical purposes some benzoic acid is still made by the sublimation of gum benzoin.

It may be prepared from aniline through the diazonium salt and benzonitrile, which is hydrolysed :

$$C_6H_5NH_2 \xrightarrow[HNO_2]{} C_6H_5N_2Cl \xrightarrow[Cu_2(CN)_2]{} C_6H_5CN \xrightarrow[H_2O]{} C_6H_5COOH.$$

Benzoic acid crystallises in needles, melting at 122°. It is only sparingly soluble in cold water, but is soluble in hot water and volatile in steam.

REACTIONS. 1. Heat a little benzoic acid in a dry tube with soda-lime. Benzene is produced.

2. To a solution of a benzoate, add hydrochloric acid. Benzoic acid is precipitated in colourless, shining leaflets or needles.

3. To a solution of a benzoate add ferric chloride solution. A pale brown precipitate of basic ferric benzoate,

$$(C_6H_5COO)_6Fe_2 . Fe_2O_3 . 15H_2O,$$

is obtained.

4. Heat a little benzoic acid with alcohol and conc. sulphuric acid ; the odour of ethyl benzoate is observed.

277. Ethyl benzoate, $C_6H_5 . COOC_2H_5$. Dissolve 50 g. of benzoic acid in 100 g. of 95 per cent. alcohol, and through this solution pass a rapid current of hydrogen chloride gas from a Kipp's generator until the weight of the solution has increased by about 4 g. (Fischer's esterification method.) The solution is now boiled under reflux for about two hours, until a drop of the liquid removed on a glass rod and mixed with a few drops of water in a test-tube gives no solid benzoic acid, but only the oily ester.

Distil off the alcohol from a water-bath, and shake the cooled residue with sodium carbonate solution until free from acid. Extract the ethyl benzoate with ether, and place the ethereal solution in a dry flask with anhydrous sodium sulphate for some hours. Decant into a dry distilling flask, recover the ether, and then distil the benzoate. The boiling point is 212°. Yield about 45 g.

Ethyl benzoate is a colourless liquid of sp. gr. 1·05 at 16°, insoluble in water, readily decomposed by alcoholic potash.

278. **Paratoluic acid,** $CH_3C_6H_4COOH$. The three isomeric toluic acids are produced when the corresponding xylenes are oxidised by boiling with dilute nitric acid.

Paratoluic acid is most easily obtained from paratoluidine by diazotising and preparing the nitrile, which is then hydrolysed :

$$CH_3C_6H_4NH_2 \xrightarrow{HNO_2} CH_3C_6H_4N_2Cl \xrightarrow{Cu_2(CN)_2} CH_3C_6H_4CN \xrightarrow[HCl]{} CH_3C_6H_4COOH.$$

It crystallises from hot water or alcohol in needles, m.p. 180°, and is volatile in steam.

279. **Benzoyl chloride,** C_6H_5COCl, is prepared by the action of phosphorus pentachloride on the dried acid :

$$C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl + POCl_3 + HCl.$$

25 g. benzoic acid is placed in a half-litre round flask, fitted with an air condenser and resting on a cold sand-bath in a good fume-chamber. 45 g. PCl_5 quickly powdered in a dry mortar is added to the acid and mixed by shaking. A vigorous reaction sets in ; much heat is developed, with evolution of HCl, and the mixture liquefies. When the reaction is over, the liquid is fractionated, using the air condenser. The distillation should be repeated. $POCl_3$ boils at 107·23°.

Benzoyl chloride is a colourless liquid, b.p. 199°. The vapour is irritating to all mucous membranes, being hydrolysed by water into benzoic and hydrochloric acids :

$$C_6H_5COCl + H_2O \rightarrow C_6H_5COOH + HCl.$$

Alcohol similarly yields ethyl benzoate, when NaOH is added slowly to a mixture of alcohol and benzoyl chloride. Two important reactions are illustrated in the next two experiments.

280. Phenyl benzoate, $C_6H_5COOC_6H_5$ (Schotten-Baumann reaction). Dissolve 1 g. phenol in 5 c.c. NaOH solution (2N reagent), add 1 c.c. benzoyl chloride and shake, warming if necessary, until the phenyl benzoate separates as an oil which solidifies on cooling. Filter, wash and crystallise from alcohol. Yield, quantitative. M.p. 66°.

281. Benzamide, $C_6H_5 . CONH_2$. Grind 10 g. of ammonium carbonate to fine powder in a mortar, add 10 g. of benzoyl chloride, and mix thoroughly until all action ceases. Benzamide is formed :

$$C_6H_5 . COCl + (NH_4)_2CO_3 = C_6H_5 . CONH_2 + NH_4Cl + CO_2 + H_2O.$$

Add water to remove ammonium salts, filter, wash and crystallise from hot water or a little alcohol. Benzamide crystallises in pearly flakes melting at 130°.

REACTION. Boiled with NaOH solution, ammonia is liberated. The liquid on acidifying with HCl gives a white ppt. of benzoic acid.

282. Mandelic acid, $C_6H_5CH(OH)COOH$. The nitrile, $C_6H_5CH(OH)CN$, is first prepared from benzaldehyde by the addition of hydrogen cyanide.

20 g. of benzaldehyde and 14 g. of finely powdered 98 per cent. KCN (or the equivalent amount of the purest available) are placed in a small flask cooled in a bath of crushed ice. 20 c.c. conc. HCl is added slowly from a dropping funnel, mixing the contents of the flask well without lifting it from the ice. When all the acid is added, the flask is left in the ice for at least one hour, with frequent shaking. The liquid is then mixed with 4–5 times its volume of cold water, separated and washed with more water, and run into a small flask. Yield about 24 g. The nitrile is rather unstable and should be hydrolysed without delay.

To this end the oil is placed in a porcelain dish with 50–60 c.c. conc. HCl, and slowly evaporated until crystals begin to form on the surface. Hot water is now added to dissolve the solid, and the liquid is filtered and cooled, extracted with ether, the ether

evaporated and the residual mandelic acid dried by warming in a small dish. Crystallised from benzene it forms colourless rhombic plates or prisms, m.p. 118°. Yield, 26 g.

283. Cinnamic acid, $C_6H_5CH:CHCOOH$ (Perkin's reaction). 20 g. benzaldehyde, with 30 g. acetic anhydride and 10 g. fused sodium acetate in powder, are heated together in a round flask to 180° for 8–9 hours. The flask is fitted with an air condenser. If the heating cannot be completed in one period, the top of the condenser should be closed with a $CaCl_2$ tube. The aldehyde first forms an aldol-addition compound which is then dehydrated :

$$C_6H_5CHO + CH_3COONa \rightarrow C_6H_5CHOH \cdot CH_2COONa$$

$$C_6H_5CH:CH \cdot COONa \leftarrow \text{—} - H_2O.$$

After 9 hours boiling the mixture is allowed to cool, mixed with hot water in a large flask, and steam-distilled to remove unchanged benzaldehyde. The remaining liquid is decanted from some dark-coloured oil, the latter boiled with more water, and the whole solution decolorised by boiling with animal charcoal. Cinnamic acid crystallises from hot water in fine needles, m.p. 133°. It is very slightly soluble in cold water, but may be crystallised from alcohol. Yield, 16 g.

REACTIONS. The salts of cinnamic acid resemble benzoates, but are unsaturated.

1. Bromine water is decolorised, dibromohydrocinnamic acid being formed.

2. Permanganate solution is decolorised, oxidising the acid to the glycol, then to benzaldehyde and benzoic acid.

3. Ferric chloride gives a yellow ppt. of cinnamate.

284. Hydrocinnamic acid, $C_6H_5CH_2CH_2COOH$, 3-phenyl propan-1-oic acid, is easily prepared by allowing a solution of sodium cinnamate to stand in contact with a slight excess of sodium amalgam. The free acid is very soluble, and crystallises in needles, m.p. 47°.

285. Phenol (Carbolic Acid, C_6H_5OH), is obtained from the middle oil of coal-tar distillation, at 170° to 230°, and is separated

from naphthalene, the other main component of the oil, by dissolving it out as its sodium salt. It can also be obtained from the sodium salt of benzene sulphonic acid by fusion with caustic soda at 300° :*

$$C_6H_5SO_3Na + NaOH = C_6H_5ONa + NaHSO_3.$$

It is also manufactured in large quantities from chlorobenzene by heating with soda to 350° under high pressure : the chlorine is replaced by the ONa group. The sodium phenoxide obtained by these methods is decomposed with sulphuric acid, and the phenol separated and distilled :

$$2C_6H_5ONa + H_2SO_4 = 2C_6H_5OH + Na_2SO_4.$$

Phenol forms colourless crystals ; m.p. 43°, b.p. 183°. On exposure to the air it acquires a light pink colour through oxidation. It has a strong irritant action on the skin, and is a powerful disinfectant. It dissolves readily in water giving an acid solution. It forms salts with caustic alkalis, but not with carbonates, and the salts are decomposed by carbon dioxide.

REACTIONS. 1. To a solution of phenol add some bromine water. A white crystalline precipitate of 2 : 4 : 6-tribromophenol is obtained, m.p. 93°. Phenol is estimated in this way (463).

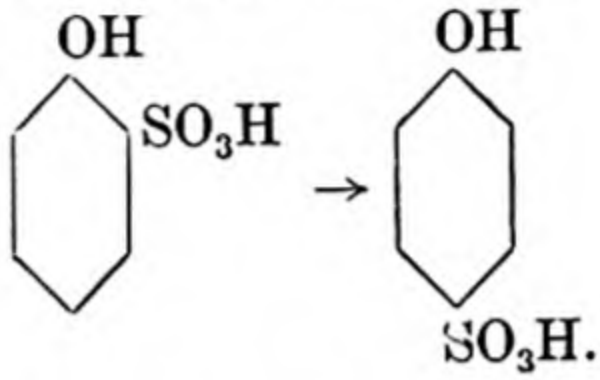
2. Ferric chloride solution gives a violet coloration, destroyed by mineral acids and by acetic acid.

3. Dissolve a little sodium nitrite in a few c.c. of conc. sulphuric acid by gently warming and add a small quantity of phenol. A brown coloration, rapidly changing to blue, is produced. Pour the liquid into water ; the colour becomes red, changing again to blue on the addition of an alkali (Liebermann's nitroso reaction).

Phenol is used in the manufacture of salicylic acid, picric acid, phenacetin, and other drugs, dyestuffs and synthetic resins such as Bakelite. The dilute aqueous solution is a strong antiseptic, though in this respect phenol is far surpassed by some of its homologues.† Pentachlorophenol is a valuable antiseptic and preservative for timber, textiles and other materials.‡‡

* Othmer and Leyes, *Ind. Eng. Chem.*, **33,** 158 (1941).
† Coulthard, Marshall and Pyman, *J.C.S.* 1930, 280.
‡ Carswell and Nason, *Ind. Eng. Chem.*, **30,** 622 (1938).

Sulphonation of phenol. When phenol is dissolved in cold sulphuric acid, sulphonation results with formation of the ortho- and para-sulphonic acids, the latter predominating. Heat transforms the orthosulphonic acid into the para-isomer :



Nitration of phenol. Phenol is easily nitrated, the nitro-groups being symmetrically disposed in the molecule, like the bromine atoms in tribromophenol. Nitration with dilute acid gives a mixture of the *o*- and *p*-nitroderivatives.

286. Orthonitrophenol. Dissolve 80 g. of sodium nitrate in 200 c.c. of water contained in a half-litre flask : mix in slowly 100 g. of conc. H_2SO_4 and cool in running water. To this add in small quantities, with constant stirring, a mixture of 50 g. of phenol and 5 g. of alcohol, melted by warming slightly. The mixture must be well shaken and cooled. It becomes dark brown in colour, and the nitro-phenols separate as a dark coloured viscid mass. Allow to stand for several hours, shaking at intervals, and then, after pouring off the acid liquid as far as possible, distil the oil in a current of steam. The orthonitrophenol passes over, and solidifies in long yellow needles, melting at 45°. Yield, about 25–30 g.

287. Paranitrophenol. The liquid remaining in the flask contains the non-volatile *p*-nitrophenol. Pour the aqueous layer through a filter, leaving the tar in the flask. Extract the tar several times with small quantities of boiling water, and add this to the main portion. The whole is then decolorised by boiling with 20 g. of animal charcoal for 20–30 minutes, filtered hot through a fluted filter, concentrated and allowed to cool. The paranitrophenol crystallises in long, almost colourless, needles, melting at 114°. Yield, about 8–10 g.

288. Picric acid (2 : 4 : 6-trinitrophenol). Dissolve 10 g. of phenol in 20 g. of conc. sulphuric acid by warming in a small flask. Phenolsulphonic acid is produced. Add this little by little, when cold, to 50 g. nitric acid (sp. gr. 1·41) in a half-litre flask. Much heat is generated, and abundant red fumes evolved. Heat the mixture on the steam pan for two hours, with frequent shaking. On cooling, picric acid separates as a yellow crystalline solid. Dilute the mixture with 150–200 c.c. of cold water, filter at the pump, wash with cold water, in which the acid is sparingly soluble, and recrystallise from hot water. Picric acid forms yellow needles, melting at 122·5°. The yield is about 15 g

Picric acid is a monobasic acid, with a dissociation constant about ten times that of phenol. It decomposes carbonates, giving a soluble sodium salt; the potassium salt is sparingly soluble. It dyes wool and silk yellow from an acid bath, and stains the skin and hair, but the colours are not fast. It is a powerful explosive (lyddite), but the metallic salts are easily detonated, and it is now replaced by the safer T.N.T. (247).

The influence of the nitro group in modifying the acidic or basic character of phenols and amines is illustrated in the following table: *

DISSOCIATION CONSTANTS OF PHENOLS AND AMINES AT 25°

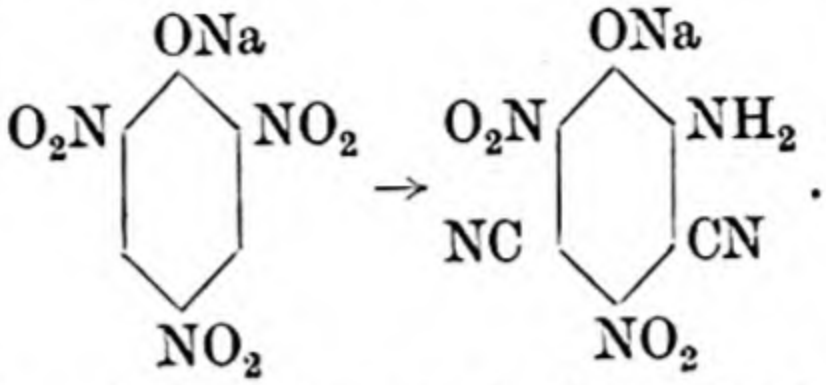
Phenols		Amines	
Phenol	$1{\cdot}09 \times 10^{-10}$	Aniline	$5{\cdot}7 \times 10^{-10}$
o-Nitrophenol	$6{\cdot}8 \times 10^{-8}$	*o*-Nitroaniline	$1{\cdot}0 \times 10^{-14}$
m- ,,	$3{\cdot}9 \times 10^{-9}$	*m*- ,,	$4{\cdot}0 \times 10^{-12}$
p- ,,	$7{\cdot}0 \times 10^{-8}$	*p*- ,,	$1{\cdot}0 \times 10^{-12}$
Picric acid	$1{\cdot}6 \times 10^{-1}$		

REACTIONS. 1. A solution of a picrate warmed with glucose and NaOH has one *o*-NO_2 group reduced forming picramic acid (2-amino-4 : 6-dinitrophenol). A deep red colour is produced.

2. Warmed with Na_2CO_3 solution and excess of KCN, a purple

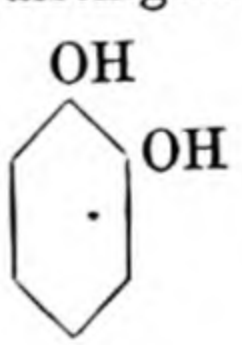
* W. A. Waters, *Phys. Aspects of Org. Chem.* 208 (1935).

colour is produced, owing to the formation of the salt of isopurpuric acid :

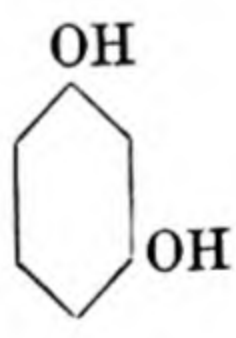


3. Picric acid unites with many hydrocarbons to form beautifully crystalline and coloured picrates, having definite melting points. They result on mixing alcoholic solutions of the two substances. Naphthalene picrate, $C_{10}H_8 . C_6H_2(NO_2)_3OH$, forms lustrous yellow needles, m.p. 149·5°. Anthracene picrate crystallises in red needles, m.p. 138°. Such compounds are decomposed by warming with NH_4OH solution, which dissolves the picric acid and leaves the hydrocarbon.

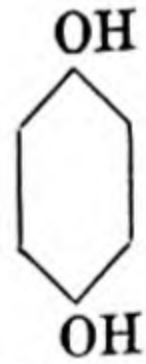
289. Dihydroxybenzenes, $C_6H_4(OH)_2$. There are three dihydroxy benzenes, obtained by alkali fusion of the corresponding disulphonic, phenolsulphonic or chloro- or iodo-phenol salts at 180–280°. Many ortho and para di-derivatives of benzene are transposed to meta-dihydroxy salts on alkali fusion. The three compounds are thus distinguished :



Pyrocatechol



Resorcinol



Quinol (Hydroquinone)

	Pyrocatechol	Resorcinol	Quinol (Hydroquinone)
M.p. - -	104°	119°	169°
B.p. - -	245°	276°	sublimes
Lead acetate -	white ppt. $PbC_6H_4O_2$	no ppt.	no ppt.
Ferric chloride -	green	deep violet	yellow, quinone (note odour)
Bromine water -	no ppt.	*sym*-Tribromo-resorcinol, m.p. 111°	no ppt.

The *o*- and *p*-compounds are strong reducing agents, and are used as photographic developers.

Resorcinol, heated with phthalic anhydride (a small crystal of each) and a pellet of $ZnCl_2$, gives the red condensation product *fluorescein*. On cooling and dissolving in NaOH solution, the soluble Na salt is formed. It has a strong red-green fluorescence, best seen in dilute solution. Compare 222, 3.

290. **Salicylic acid** (*o*-hydroxybenzoic acid), $C_6H_4(OH) . COOH$, is prepared by acting on sodium phenoxide with dry carbon dioxide at ordinary temperatures so long as absorption takes place. Phenyl sodium carbonate is produced :

$$C_6H_5 . ONa + CO_2 = C_6H_5 . O . COONa.$$

This is then heated for several hours in autoclaves to about 140° (Kolbe-Schmidt method), and is thus converted into the isomeric sodium salicylate, which remains as a dry powder :

$$C_6H_5 . O . COONa \rightarrow C_6H_4(OH) . COONa.$$

This is dissolved in water, the acid precipitated with hydrochloric acid, and purified by recrystallisation. It crystallises in colourless needles, melting at 159°, and is sparingly soluble in cold water, more easily in hot water, and readily soluble in alcohol and ether.

Salicylic acid is a valuable antiseptic, used as a preservative and in medicine.

REACTIONS. 1. Heat a little salicylic acid with soda-lime. Phenol is produced (compare benzoic acid, 276, 1).

2. To a solution of the acid add bromine water. A pale yellow precipitate of dibromosalicylic acid is obtained.

3. Ferric chloride gives a red-violet colour with neutral solutions of salts, more violet with the free acid, and also in alcoholic solution (distinction from phenol). The colour is destroyed by mineral acids or by acetic acid.

4. Salicylic acid and methyl or ethyl alcohol, heated with a little H_2SO_4, gives the esters, recognisable by their pleasant odours.

Oil of wintergreen contains the methyl ester, which forms about 90 per cent. of the natural oil. It may be prepared like ethyl benzoate, or by heating a mixture of 25 g. methyl alcohol, 25 g. salicylic acid, and 15 g. sulphuric acid for an hour under reflux, and then distilling. It boils at 224°. It is used in flavouring and in the preparation of liniments.

Salol, $C_6H_4(OH)COOC_6H_5$, is the phenyl ester, and is obtained in colourless, tasteless crystals, melting at 43°. It is scarcely soluble in cold water, easily in alcohol or ether, and is used as an internal antiseptic and antirheumatic, being hydrolysed in the intestines, where the fluids are alkaline.

Aspirin is acetyl salicylic acid, $C_6H_4(COOH)O \cdot CO \cdot CH_3$, and may be prepared by boiling with acetic anhydride, or heating the acid with acetyl chloride in sealed tubes to 80–90°. A crystalline mass is obtained, which is washed with a little cold water and recrystallised from chloroform. It forms fine colourless needles, melting at 135°, slightly soluble in water. It is largely used as a drug, replacing salicylic acid in the treatment of rheumatism and neuralgia.

291. Benzophenone, $(C_6H_5)_2CO$. Friedel and Crafts reaction. When benzoyl chloride and benzene are mixed together in presence of anhydrous aluminium chloride, condensation occurs with elimination of hydrogen chloride.

$$C_6H_5COCl + C_6H_6 \rightarrow C_6H_5COC_6H_5 + HCl.$$

In a half-litre round flask place 20 g. benzene, 25 g. benzoyl chloride and 90–100 c.c. carbon bisulphide. The last acts as a diluent and ensures that the mixture shall have a low boiling point. To the mixture add in portions with continual shaking 20 g. anhydrous $AlCl_3$ which is weighed and kept in a corked test-tube. Now attach the flask to a reflux condenser and warm gently on a water bath, arranging for the absorption of HCl as in bromination (243) unless there be a good draught. Keep the mixture boiling gently until the evolution of gas ceases, which will take $2\frac{1}{2}$–3 hours, and then distil the CS_2 and some excess benzene from the water-bath.

Pour the still fluid residue on to some crushed ice, rinsing out the flask with a little cold water and some HCl if necessary. Blow steam through the liquid in a flask, and after cooling, extract the whole with ether. Wash the ether extract with soda solution, then with water, and dry overnight with Na_2SO_4. Filter, distil the ether and fractionate the residue. Yield, 20 g.*

Benzophenone forms colourless crystals, m.p. 48·5°, b.p. 306·1°, easily soluble in alcohol or ether, insoluble in water. PCl_5 converts it into the dichloride, $(C_6H_5)_2CCl_2$, sodium amalgam in alcohol reduces it to benzhydrol, $(C_6H_5)_2CHOH$ (270), while HI reduces it to the hydrocarbon diphenylmethane, $(C_6H_5)_2CH_2$, m.p. 26°.

Benzophenone oxime, $(C_6H_5)_2C : N . OH$, is prepared by mixing cold solutions of 2·5 g. benzophenone in 20 c.c. alcohol, and 2·5 hydroxylamine hydrochloride in 5 c.c. water with 5 g. KOH in 5 c.c. water. The whole is boiled under reflux for two hours, and mixed with 50 c.c. cold water to precipitate unchanged ketone. From the filtered solution the oxime is precipitated by acidifying with dilute H_2SO_4, and crystallised from alcohol. It forms colourless crystals, m.p. 141°.

292. The Beckmann rearrangement. Oximes are transposed into the isomeric imides when treated with certain reagents (Beckmann, 1886) :

$$(C_6H_5)_2C : NOH \rightarrow C_6H_5CONHC_6H_5.$$

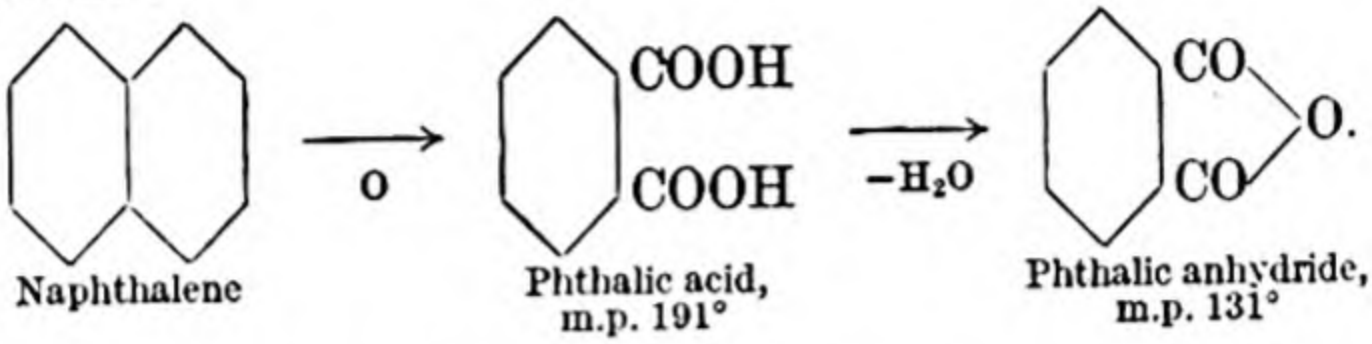
Dissolve 1 g. of benzophenone oxime in 15 c.c. dry ether, and while cooling add gradually with shaking 1·5 g. finely powdered PCl_5. When the reaction is over distil the ether, and precipitate the benzanilide by careful addition of cold water. Filter, wash and crystallise from alcohol.

Benzanilide crystallises from alcohol in colourless leaflets, m.p. 160°. In reactions it resembles acetanilide (252).

293. Phthalic acid, $C_6H_4(COOH)_2$. There are three isomeric benzene dicarboxylic acids. The only important one, and the only one which gives an anhydride, is the ortho-acid, which is

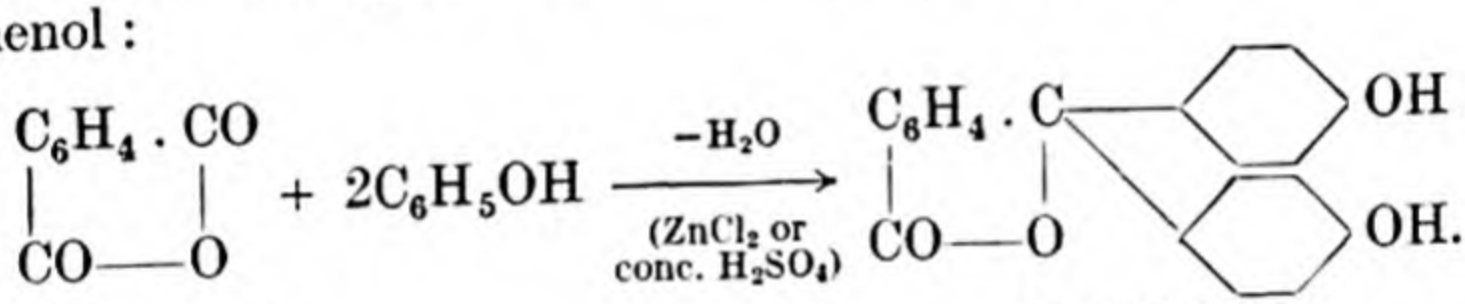
* G. Egloff and others, *Chem. Reviews*, 1937, **20**, 345.

now obtained by the catalytic oxidation of naphthalene with the aid of certain rare metal oxides at 250°. Since the acid loses water just above its m.p. of 191°, the actual product is the anhydride :



Naphthalene — Phthalic acid, m.p. 191° — Phthalic anhydride, m.p. 131°

294. Phenolphthalein is the simplest representative of a series of colouring matters made by condensing phthalic anhydride with two molecules of a mono- or poly-hydroxy phenol. A carbonyl oxygen atom in the anhydride is removed with the hydrogen atoms para- to the OH group in two molecules of a phenol :



Phthalic anhydride — Phenolphthalein

(Compare 222, 3, and 289). Phenolphthalein is a colourless solid almost insoluble in water, soluble in alcohol. It is soluble in alkalis giving intensely red-coloured solutions, and is used as an indicator in acidimetry (407).

ALKALOIDS

295. The term alkaloid is applied to certain nitrogenous organic bases of more or less complex constitution, which occur in plants and have well-defined physiological properties. They are usually optically active, insoluble or sparingly soluble in water, soluble in most organic solvents, and give salts which are more or less easily soluble. Some are volatile liquids, and can be steam-distilled from the plant, as nicotine from tobacco : others are crystalline solids that are best extracted by the aid of solvents, as quinine from quinia bark.

The alkaloids are precipitated from solutions of their salts by

caustic soda; some, like morphine, redissolve in excess of the alkali. All are precipitated from solution by certain general reagents, as phosphomolybdic acid, phosphotungstic acid, tannic acid, picric acid, $HgI_2 . 2KI$, $BiKI_4$, and iodine in potassium iodide. The compounds so obtained assist by their colour and texture in the identification of the alkaloid.

296. **Quinine**, $C_{20}H_{24}N_2O_2$, is a tertiary, di-acid base, crystallising in shining white needles, melting at 177°. It is sparingly soluble in water, the solution being alkaline to litmus, and laevorotatory. It is of great value as a febrifuge in the treatment of intermittent fevers, and is more potent than any of its synthetic substitutes.

REACTIONS. 1. Solutions of the sulphate, nitrate, acetate show a blue fluorescence, destroyed by halogen hydrides.

2. NaOH solution precipitates quinine, insoluble in excess.

3. To a solution of the sulphate add chlorine or bromine water, and then ammonia; an emerald green colour is produced, changed to red by acids.

297. **Cinchonine**, $C_{19}H_{22}N_2O$, occurs with quinine and other alkaloids in cinchona bark. It is very sparingly soluble in water and in cold alcohol, more soluble in hot alcohol, or in a mixture of this with chloroform. It is dextrorotatory. The salts are more soluble than the corresponding salts of quinine, and are not fluorescent. Physiologically they are less active than quinine salts.

REACTIONS. 1. NaOH or Na_2CO_3 precipitates the base from its salts, insoluble in excess. $NaHCO_3$ gives the same precipitate.

2. Cl water gives no colour, but on adding NH_4OH a yellowish white precipitate is produced.

3. K_4FeCy_6 gives a yellowish flocculent precipitate of the ferrocyanide, soluble on warming gently with excess of the reagent. On cooling, it crystallises in golden-yellow scales, or long needles. These should be examined under the microscope.

298. **Morphine**, $C_{17}H_{19}NO_3$, is the principal alkaloid in opium. It crystallises with one molecule of water, which it loses at 120°, is very sparingly soluble in water, and only slightly in alcohol. Its best solvent is amyl alcohol. The solutions are laevorotatory.

REACTIONS. Use a solution (1–2 per cent.) of the hydrochloride.

1. NH_4OH ppts. the base, difficultly soluble in excess, but readily soluble in caustic alkalis.

2. Na_2CO_3 or $NaHCO_3$ gives the same ppt. insoluble in excess.

3. HNO_3 gives an orange-red colour, which is not changed to violet by sodium thiosulphate (distinction from brucine).

4. $FeCl_3$ gives a blue colour, destroyed by acids or by heat, though it reappears on cooling.

5. Iodic acid gives a brown colour, partly due to free iodine. This may be detected with starch solution.

The last three colour tests may be made with specks of the solid, and a drop of the reagent on a white plate.

Heroin is the diacetyl derivative of morphine. Its reactions are similar to those of morphine.

299. **Brucine**, $C_{23}H_{28}N_2O_4$, is found along with strychnine in various kinds of *strychnos*. It crystallises with four molecules of water, is sparingly soluble in cold water, and has an intensely bitter taste. It is readily soluble in alcohol, and may thus be separated from strychnine, which is insoluble in cold absolute alcohol. Alcohol solutions are laevorotatory.

REACTIONS. 1. NaOH or Na_2CO_3 precipitates brucine from solutions of its salts, insoluble in excess.

2. Conc. HNO_3 gives an intensely red solution, becoming yellow on warming. This may be done by spotting on a white plate. On adding $SnCl_2$ or $Na_2S_2O_3$ to the yellow solution, or rubbing the spot with a crystal of $Na_2S_2O_3$ an intense violet colour is produced (distinction from morphine).

3. Conc. H_2SO_4 gives a pale-rose colour, changing slowly to yellow. A trace of HNO_3 stirred into this gives an intense orange-red colour.

4. $Hg_2(NO_3)_2$ free from HNO_3 gives a colourless solution, which on warming develops a fine carmine colour (distinction from strychnine, which gives no colour).

300. **Strychnine**, $C_{21}H_{22}N_2O_2$, occurs in various species of *strychnos*, together with brucine. It forms colourless rhombic prisms, is almost insoluble in water and alcohol, alkaline in

reaction and of intensely bitter taste. It dissolves easily in chloroform. Most of the salts are soluble in water and alcohol, and are very poisonous.

REACTIONS. 1. Caustic alkali or carbonate precipitates the base, insoluble in excess.

2. NH_4OH gives the same precipitate, which however dissolves in excess and crystallises in needles.

3. $HgCl_2$ gives a white precipitate which dissolves on boiling, but recrystallises in needles on cooling.

4. Dissolved in conc. H_2SO_4 and mixed or rubbed with a fragment of any oxidiser like $K_2Cr_2O_7$, MnO_2, $KMnO_4$, a fine blue-violet colour is produced, which changes to red and then to reddish-yellow. Brucine, morphine or quinine interfere with this reaction.

5. Sulphovanadic acid (Mandelin's reagent) added to a solution in H_2SO_4 gives an intense blue colour, changing to violet and then to red on standing or warming.

The **Tropane** series of alkaloids includes some important compounds.

Atropine, $C_{17}H_{23}NO_3$, the poison of the Deadly Nightshade (*Atropa belladonna*), is the ester of *dl*-tropic acid and the secondary alcoholic base tropine, $C_7H_{13}N$. CHOH, into which it is readily hydrolysed. It crystallises in prisms, m.p. 118°. Its solutions are alkaline, of a bitter taste, and possess mydriatic properties, dilating the pupil of the eye. The sulphate,

$$(C_{17}H_{23}NO_3)_2H_2SO_4 . H_2O,$$

is used in ophthalmic surgery.

Hyoscyamine, the poisonous principle of Henbane (*Hyoscyamus niger*), is the laevo isomeride of atropine, hydrolysing into tropine and *l*-tropic acid. It crystallises in needles, m.p. 109°, and its solutions also have mydriatic properties. It is converted into atropine (racemised) by the action of alkali.

Cocaine, $C_{17}H_{21}NO_4$, is the most important alkaloid in Peruvian *coca* leaves, and the only one possessing marked physiological action. It is a valuable local anaesthetic, much used in dental and ophthalmic surgery.

SECTION II

QUALITATIVE ANALYSIS

INSTRUCTIONS TO STUDENTS

In the section on Qualitative Analysis those reactions of the anions and cations having no bearing on the subsequent analysis have been omitted. The principal products of the reactions are given, but the equations, except the more difficult, have been left to be entered by the student.

Reference should be made to the tables in the appendix, which indicate the solubilities of the principal salts, and to par. 89 on solubility products, in order to obtain a clear understanding of the reactions on which the analysis depends. From the reactions given, other methods of separation should also be devised by the student (see 93).

In the analysis of a substance, a preliminary examination should be made before the separation of the cations into groups. This examination consists of a few dry tests together with tests for certain anions, some of which, if present, will necessitate a modification of the group separation. Such are borates, fluorides, phosphates and organic substances.

The final detection of the anions can be left conveniently to the end of the analysis. As there is no definite separation into groups, a list of those which have not been definitely shown to be absent or present should be made and each tested for or confirmed separately.

In all operations, careful note of all results should be made and conclusions suggested. For example, if it be necessary to dissolve the substance in nitric acid, the production of reddish-brown fumes may indicate a free metal such as copper, or a reducing agent.

The student should not omit to record an observation because at the time it does not convey any information to him.

The increasing importance of organic reagents in qualitative and quantitative analysis has caused the introduction of a selected few among the reactions given in the following pages. Dimethylglyoxime is a well-known reagent for nickel, but in many cases the reagent is not specific for a particular ion and considerable care and experience are necessary in carrying out the tests. Further, many of these are extremely delicate and would be useless except for very accurate analyses. Some of them can be carried out as spot tests on filter paper, on a porcelain tile or on a microscope slide.

REACTIONS OF THE CATIONS

THE SILVER GROUP

Cations whose chlorides have a low solubility product. (Note, lead chloride is slightly soluble in cold water, much more readily in hot water.)

301. Lead. DRY REACTION. Heated on charcoal, lead compounds are readily reduced to the metal, which is soft, malleable, and easily marks paper.

REACTIONS IN SOLUTION. **$Pb^{..}$**. Use lead acetate, $Pb(COOCH_3)_2$, or lead nitrate, $Pb(NO_3)_2$.

1. **Hydrochloric acid** gives a heavy white precipitate of lead chloride, $PbCl_2$, soluble in hot water, crystallising in white needles on cooling. $PbCl_2$ is soluble in concentrated HCl, re-precipitated on dilution.

2. **Sulphuretted hydrogen** produces a black precipitate of lead sulphide, PbS, converted by boiling with dilute nitric acid into nitrate and sulphate. In strongly acid solutions the precipitate is first reddish brown lead sulphochloride, ClPb . S . PbCl.

3. **Sulphuric acid** precipitates white lead sulphate, $PbSO_4$, slightly soluble in water, insoluble in 50 per cent. alcohol. It is soluble in a solution of ammonium acetate or tartrate, or in concentrated potassium hydroxide or hydrochloric acid.

4. **Sodium hydroxide** produces a white precipitate of lead hydroxide, $Pb(OH)_2$, soluble in excess forming sodium plumbite, $Pb(ONa)_2$ or $Pb(OH)ONa$.

5. **Potassium iodide** gives a yellow crystalline precipitate of lead iodide, PbI_2, soluble in hot water, and recrystallising in shining yellow plates.

6. **Potassium chromate** precipitates lead chromate (chrome yellow), $PbCrO_4$, soluble in dilute nitric acid but not in acetic.

7. **Sodium carbonate** forms a white precipitate of basic lead carbonate, $x\ PbCO_3 . y\ Pb(OH)_2$.

8. **Spot test.** Moisten a filter paper with a drop of ammoniacal hydrogen peroxide, add a drop of the solution to be tested and hold the paper in steam for a minute. The lead is oxidised to lead dioxide and the excess of H_2O_2 is decomposed. One drop of the reagent (·5 per cent. solution of **benzidine** in 10 per cent. acetic acid) will give a blue colour. The test is given also by other metals which form compounds having oxidising properties (*e.g.* Cr, Mn, Ce, etc.).

9. Add one drop of a solution of 1 to 2 mg. of **diphenylthiocarbazone** in 100 c.c. of carbon tetrachloride to a drop of the solution to be tested. A brick-red compound soluble in the CCl_4 is formed with heavy metals, but in presence of potassium cyanide and an alkali tartrate the test is specific for lead.

302. Silver. Dry Reaction. Heated on charcoal, silver compounds are readily reduced to the metal, which may be obtained as a bead at a high temperature. The bead is bright, white and hard.

Reactions in Solution. $Ag^{\cdot}$. Use silver nitrate, $AgNO_3$.

1. **Hydrochloric acid** gives a white, curdy precipitate of silver chloride, AgCl, insoluble in nitric acid, slightly soluble in hydrochloric acid or alkali chlorides forming the complex anion $[AgCl_3]''$. It is readily soluble in ammonia, potassium cyanide or thiosulphate solutions, forming respectively the complex ions $[Ag(NH_3)_2]^{\cdot}$, $[Ag(CN)_2]'$ and $[Ag_2(S_2O_3)_3]''''$. The last breaks up on boiling, with precipitation of black Ag_2S and sulphur (341, 3).

2. **Sulphuretted hydrogen** precipitates black silver sulphide, Ag_2S, soluble in hot nitric acid or in KCN solution.

3. **Ammonium hydroxide** at first forms the unstable white hydroxide, AgOH, which at once decomposes to yield the brown oxide, Ag_2O. This dissolves in excess of ammonia forming silver diammine hydroxide :

$$Ag_2O + 4NH_3 + H_2O \rightarrow 2[Ag(NH_3)_2]^{\cdot} + 2OH'.$$

4. **Sodium hydroxide** produces a brown grey precipitate of silver oxide, Ag_2O, readily soluble in ammonia, giving the above silver diammine-hydroxide.

5. **Potassium chromate** gives a brick-red precipitate of silver chromate, Ag_2CrO_4, readily soluble in dilute nitric acid, decomposed by solutions of alkali chlorides into silver chloride and a soluble chromate (see use as indicator, **464**).

6. **Sodium carbonate** gives a white precipitate of silver carbonate, turning yellow on boiling owing to partial decomposition into oxide.

7. ***p*-Dimethylaminobenzalrhodanine,** in ·03 per cent. solution in acetone, added to a drop of a silver solution on a tile, followed by two drops of dilute nitric acid, gives a red colour. A drop of KCN solution prevents interference by mercury and a drop of dilute HCl prevents interference by copper. The test is much more delicate than the chloride test.

303. Mercury. Dry Reaction. Many mercury salts volatilise unchanged on heating, while others decompose, so that when heated in a dry tube they may give a white sublimate, $HgCl_2$, a yellow sublimate, HgI_2, or a sublimate of mercury, HgO, $Hg(NO_3)_2$, etc. If heated with sodium carbonate, all mercury salts yield the metal.

Reactions in Solution. **$Hg^{\cdot}$.** Use a solution of mercurous nitrate, $HgNO_3$.

1. **Hydrochloric acid** precipitates white mercurous chloride, Hg_2Cl_2 (calomel), soluble in aqua regia. It is turned black by ammonia forming a mixture of mercury and mercuric ammonium chloride, $Hg + NH_2HgCl$.

2. **Sodium hydroxide** gives a black precipitate of mercurous oxide, Hg_2O, containing HgO and mercury. The hydroxide probably does not exist.

3. **Ammonium hydroxide** produces a black precipitate of the metal together with basic mercuric ammonium nitrate,

$$2Hg + HgO \,.\, NH_2Hg \,.\, NO_3.$$

4. **Sodium carbonate** gives a black precipitate as in 2.

5. **Potassium chromate** forms a dark-red precipitate of mercurous chromate, Hg_2CrO_4, which decomposes on ignition, leaving chromium sesquioxide, Cr_2O_3 (see estimation, 501 C).

OXIDATION OF MERCUROUS SALTS.

6. Mercurous ions are easily oxidised to mercuric ions. Mercurous chloride dissolves in chlorine water or aqua regia, forming the soluble mercuric chloride, $HgCl_2$. Mercurous ions are readily reduced to mercury by stannous chloride, which is oxidised to stannic chloride.

$$2Hg^{\cdot\cdot} + Sn^{\cdot\cdot} \rightarrow 2Hg^{\cdot} + Sn^{\cdot\cdot\cdot\cdot}.$$

$$2Hg^{\cdot} + Sn^{\cdot\cdot} \rightarrow 2Hg + Sn^{\cdot\cdot\cdot\cdot}.$$

SEPARATION OF THE SILVER GROUP

The separation and detection of the cations of this group depend upon :

(*a*) The solubility of lead chloride in hot water, silver and mercurous chlorides being insoluble ;

(*b*) The solubility of silver chloride in ammonium hydroxide, mercurous chloride being insoluble.

(*c*) The formation of the black substance which mercurous chloride yields with ammonia.

THE COPPER GROUP

Cations whose sulphides have a low solubility product and are precipitated in presence of dilute acids.

304. Mercuric compounds. DRY REACTIONS. (See 303.)

REACTIONS IN SOLUTION. $Hg^{\cdot\cdot}$. Use mercuric nitrate, $Hg(NO_3)_2$, or chloride, $HgCl_2$. To a portion of the solution add hydrochloric acid ; note the result. Repeat this procedure with the other metals of the group.

1. **Sulphuretted hydrogen** produces a black precipitate of mercuric sulphide, HgS, insoluble in nitric or hydrochloric acid, but readily soluble in aqua regia. It is changed by nitric acid to a white substance, $Hg(NO_3)_2 . 2HgS$. In strongly acid solutions of mercuric salts the precipitate is first white, then yellow, reddish brown, and finally black, owing to the formation of compounds of the mercuric salt and mercuric sulphide, $xHgCl_2 . yHgS$.

2. **Sodium hydroxide** precipitates yellow mercuric oxide, HgO.

3. **Ammonium hydroxide** gives a white precipitate of mercuric ammonium chloride, NH_2HgCl.

4. **Potassium iodide** produces a bright red precipitate of mercuric iodide, HgI_2, soluble in excess of mercuric chloride, or of potassium iodide to form the complex anion HgI_4''. (See Nessler's reagent, 328, 3.)

5. **Stannous chloride** gives a white precipitate of mercurous chloride, and by further reduction, grey particles of mercury (**303**, 6).

6. **Sodium carbonate** precipitates mercuric oxide.

7. A piece of bright **copper** placed in an acidified solution of a mercury salt becomes coated with a grey deposit of mercury, which on rubbing acquires a bright surface.

8. SPOT TEST. On a filter paper soaked in a freshly prepared saturated alcoholic solution of **diphenyl-carbazide** place one drop of the solution to be tested. A violet blue fleck is produced. Pb, Cu, Sn, Cd, Ni and Co also react, but in the presence of very dilute nitric acid the test is specific for mercury in the absence of chromates and molybdates.

305. Bismuth. DRY REACTIONS. 1. Heated in a dry tube, bismuth salts are decomposed, leaving the oxide, which is orange red while hot, pale yellow on cooling.

2. Heated on charcoal, bismuth compounds are easily reduced to metal, which has a slight red tinge and is brittle. A yellow incrustation of the oxide is also formed.

REACTIONS IN SOLUTION. **Bi'''**. To a small quantity of bismuth nitrate, $Bi(NO_3)_3$, or bismuth chloride, $BiCl_3$, add water. A white oxy-salt is formed and the solution is acid. Obtain a clear solution by filtration or by adding hydrochloric acid.

1. **Sulphuretted hydrogen** gives a dark brown precipitate of the sulphide, Bi_2S_3, soluble in nitric acid.

2. **Ammonium hydroxide** precipitates white bismuth hydroxide, $Bi(OH)_3$, insoluble in excess. The precipitate is turned black by a solution of sodium stannite (310, 3).

3. Excess of **water** causes precipitation of a white oxysalt (as BiOCl).

4. **Sodium carbonate** gives a white precipitate of basic carbonate.

5. **Cinchonine** forms a double iodide, $BiI_3(C_{19}H_{22}N_2O)HI$, which appears as an orange-red coloration or precipitate on adding the reagent to a bismuth solution.

Reagent. Dissolve 1 g. of cinchonine in 100 c.c. of warm water, add 2–3 c.c. conc. HNO_3, cool and add 2 g. KI. Cu, Pb or Hg salts react with the KI, but may be detected in a **spot test.** Place two drops of the reagent on filter paper, and in the centre one drop of the solution. A white central zone indicates Hg. Surrounding this is the orange-red Bi compound, beyond it a yellow ring of PbI_2, and the outermost ring is a brown one due to free iodine from the reaction of cupric ions with the KI.

306. Copper. DRY REACTIONS. 1. Heated on charcoal, copper salts leave a black residue of copper oxide, CuO, which may be reduced, especially with fusion mixture and potassium cyanide in the reducing flame, to red scales of copper. The cyanide acts as a reducing agent, uniting with oxygen to form potassium cyanate, KOCN (234).

2. Moistened with hydrochloric acid and heated on platinum wire, copper compounds colour the flame blue. If not present as the halogen compounds, the flame is green.

3. Heated in a borax bead in the oxidising flame, the bead is green while hot, blue on cooling. In the reducing flame a red bead containing small particles of copper is obtained.

REACTIONS IN SOLUTION. **$Cu^{\cdot\cdot}$.** Use copper sulphate, $CuSO_4 . 5H_2O$. Test with hydrochloric acid.

1. **Sulphuretted hydrogen** produces a black precipitate of cupric sulphide, CuS, soluble in nitric acid and in potassium cyanide, very slightly soluble in ammonium sulphide.

2. **Ammonium hydroxide** precipitates a bluish green basic salt, $CuSO_4 . Cu(OH)_2$, which dissolves in excess, forming a deep blue solution containing the compound $Cu(NH_3)_4SO_4 . H_2O$. This blue colour is destroyed by potassium cyanide with formation of potassium cuprocyanide, $K_2[Cu(CN)_3]$.

3. **Sodium hydroxide** gives a light blue precipitate of hydroxide, $Cu(OH)_2$, insoluble in excess. It turns black on heating, giving hydrated copper oxide, $2CuO . H_2O$.

4. **Potassium cyanide** precipitates yellow cupric cyanide, $Cu(CN)_2$, which at once changes with loss of cyanogen to white cuprous cyanide, $Cu_2(CN)_2$. This dissolves in excess of KCN forming potassium cuprocyanide, $K_3[Cu(CN)_4]$. In this solution the copper is all contained in the complex anion, $[Cu(CN)_4]'''$, and there are practically no cuprous ions. Hence there is no precipitate with hydrogen sulphide (cf. Cd, **307, 4**).

5. **Potassium ferrocyanide** produces a reddish brown precipitate of ferrocyanide, $Cu_2Fe(CN)_6$, or $K_2CuFe(CN)_6$, according to the proportions used.

6. **Potassium thiocyanate** precipitates first the unstable black cupric thiocyanate, $Cu(SCN)_2$, which decomposes into white cuprous thiocyanate, $Cu_2(SCN)_2$. In presence of sulphurous acid the copper is completely precipitated as cuprous thiocyanate, insoluble in dilute acids (see estimation, **474**) :

$$2Cu(SCN)_2 + SO_3'' + H_2O \rightarrow Cu_2(SCN)_2 + 2SCN' + 2H^{\cdot} + SO_4''.$$

7. **Potassium iodide** also forms the cuprous salt, Cu_2I_2, with liberation of iodine :

$$2Cu^{\cdot\cdot} + 4I' \rightarrow Cu_2I_2 + I_2.$$

Titration of the free iodine with thiosulphate (**453**) affords a means of estimating copper. In presence of sulphurous acid no iodine is liberated, and if the copper be in excess, all the iodine is thrown out as cuprous iodide. This reaction is used for the removal of iodine before testing for the other halogens (**333, 5**).

8. **Sodium carbonate** forms a green basic carbonate, soluble in ammonia to give a deep blue solution, and in KCN forming a colourless solution.

9. **α-Benzoinoxime** (cupron), in 2 per cent. alcoholic solution, forms a green copper compound insoluble in ammonia. To use the reaction as a **spot test**, place some drops of the reagent on a small filter paper and dry it. Add a drop of the solution to be tested and expose it to ammonia. A green coloration will be produced. In ammoniacal tartrate solution other metals do not interfere.

Cuprous salts are generally colourless even in ammoniacal solution and are insoluble in water. They are soluble in dilute acids and are readily oxidised by HNO_3, H_2O_2, Br water, etc., the solution becoming blue. A solution of acetylene in acetone gives a red precipitate of cuprous acetylide, Cu_2C_2.

307. Cadmium. Dry Reaction. Heated on charcoal, cadmium compounds give a brown incrustation of the oxide, CdO.

Reactions in Solution. $Cd^{\cdot\cdot}$. Use cadmium chloride, $CdCl_2$, or sulphate, $CdSO_4$. Test with hydrochloric acid.

1. **Sulphuretted hydrogen** gives a yellow precipitate of cadmium sulphide, CdS, soluble in dilute mineral acids, and therefore not precipitated in strongly acid solutions (93).

2. **Ammonium hydroxide** precipitates white cadmium hydroxide, $Cd(OH)_2$, soluble in excess, insoluble in sodium hydroxide (distinction from zinc).

3. **Sodium carbonate** produces a white precipitate of cadmium carbonate, $CdCO_3$.

4. **Potassium cyanide** first precipitates a white cyanide, $Cd(CN)_2$, which dissolves in excess, forming potassium cadmicyanide, $K_2Cd(CN)_4$. From this solution sulphuretted hydrogen precipitates the sulphide (distinction from copper, which forms a cuprocyanide (306, 4).

308. Arsenic. Dry Reactions. 1. Heated in a dry tube, arsenic compounds volatilise, giving a sublimate. If mixed with fusion mixture and potassium cyanide and heated, a sublimate of arsenic is formed.

2. Heated on charcoal, arsenic compounds partly sublime and are partly reduced to arsenic, which then burns to the oxide.

Some arsenic vapour is mixed, however, with the oxide and may be recognised by its garlic odour.

REACTIONS IN SOLUTION. **AsO_3'''**. Use sodium arsenite, $NaAsO_2$. Test with hydrochloric acid.

1. **Sulphuretted hydrogen** gives in acid solutions a yellow precipitate of arsenic trisulphide, As_2S_3, insoluble in conc. hydrochloric acid, but soluble in ammonium sulphide, forming ammonium thioarsenite, or in ammonium carbonate.

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3.$$

With yellow ammonium sulphide, thioarsenate is produced.

$$As_2S_3 + 3(NH_4)_2S + S_2 = 2(NH_4)_3AsS_4.$$

It is also soluble in sodium hydroxide, forming a mixture of arsenite and thicarsenite.

$$As_2S_3 + 6OH' = AsS_3''' + AsO_3''' + 3H_2O.$$

From these solutions the trisulphide or pentasulphide is precipitated by hydrochloric acid.

$$2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S.$$

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 6NH_4Cl + 3H_2S.$$

$$AsS_3''' + AsO_3''' + 6H^{\cdot} = As_2S_3 + 3H_2O.$$

2. **Silver nitrate** produces from neutral solutions a yellow precipitate of silver arsenite, Ag_3AsO_3, soluble in ammonium hydroxide or nitric acid.

3. **Copper sulphate** precipitates Scheele's green, $CuHAsO_3$, soluble in ammonium hydroxide, ammonium chloride, or in nitric acid.

4. **Iodine** solution is decolorised, the arsenious acid being oxidised to arsenic acid. The solution must be kept free from hydrogen ions by adding $NaHCO_3$ or Na_2HPO_4. This is the basis of a volumetric method for the estimation of arsenious acid (**470**).

$$H_2AsO_3' + I_2 + H_2O \rightarrow H_2AsO_4' + 2I' + 2H^{\cdot}.$$

5. **Gutzeit** test. To a few c.c. of the arsenic solution in a test-tube add a little dilute sulphuric acid and some zinc. Plug the neck of the tube loosely with cotton wool to filter spray, and over

309. Antimony. DRY REACTION. Heated on charcoal, antimony compounds form a white incrustation. The metal may be obtained, but rapidly burns.

REACTIONS IN SOLUTION. **SbO_3'''.** Use antimony trichloride, or tartar emetic. Test with hydrochloric acid.

1. **Sulphuretted hydrogen** produces, in acid solutions, an orange precipitate of the sulphide, Sb_2S_3, soluble in ammonium sulphide, and in sodium hydroxide forming thio- and oxy-salts, the sulphide being reprecipitated by hydrochloric acid. The reactions are similar to those of arsenic. Antimony trisulphide is soluble in warm concentrated hydrochloric acid (distinction from As_2S_3).

2. Excess of **water** causes precipitation of the white oxychloride, SbOCl, soluble in hydrochloric acid, and in solutions of tartaric acid or tartrates (distinction from BiOCl).

3. **Silver nitrate** gives, with alkaline solutions, a black precipitate of silver oxide and silver.

4. **Sodium hydroxide** or carbonate forms a white precipitate of antimonious oxide, Sb_4O_6, soluble in excess of the former, producing sodium metantimonite.

$$4SbCl_3 + 12NaOH = Sb_4O_6 + 12NaCl + 6H_2O.$$

$$Sb_4O_6 + 4NaOH = 4NaSbO_2 + 2H_2O.$$

5. MICROSCOPE TEST. **Pyrogallol.** A crystal of this is dissolved by stirring in one drop of the slightly acid solution to be tested on a microscope slide. After a few minutes crystals of characteristic shape will separate.

6. If, in a solution of an antimony salt, a piece of zinc be placed in contact with a piece of platinum foil, the antimony will be deposited on the platinum as a brown stain.

SbO_4''' or SbO_3'. Use potassium metantimonate, $KSbO_3$. Many salts of the orthoantimonate type are unstable in solution and form metantimonates which give the ion, SbO_3'. (Compare ortho- and meta-phosphates.)

1. **Sulphuretted hydrogen** produces, in an acidified solution, an orange-red precipitate, consisting of the pentasulphide, the trisulphide and sulphur. The pentasulphide dissolves in ammonium sulphide, forming thioantimonate, $(NH_4)_3SbS_4$. It is also soluble

in sodium hydroxide, forming a mixture of sodium antimonate, thioantimonate, and hydrosulphide, but not in ammonium carbonate (distinction from arsenic).

2. **Silver nitrate** gives a white precipitate of silver antimonate, Ag_3SbO_4.

3. **Hydrochloric acid** precipitates white metantimonic acid, $HSbO_3$, soluble in excess; from this solution **sodium carbonate** reprecipitates $HSbO_3$.

4. **Rhodamine B** gives a violet coloration with antimonic compounds in the absence of Bi, Hg, molybdates or tungstates. To a few drops of the solution add two drops conc. HCl and a crystal of $NaNO_2$. This oxidises antimony compounds to the antimonic state. Add one drop of this solution to 0·5 c.c. of a 0·01 per cent. solution of the dye-stuff. The reaction may be used as a spot test.

310. Tin. Dry Reaction. Heated on charcoal, the metal is obtained with difficulty, a white incrustation being generally formed.

Reactions in Solution. $Sn^{\cdot\cdot}$. Use stannous chloride, $SnCl_2$. Test with hydrochloric acid.

1. **Sulphuretted hydrogen** precipitates dark-brown stannous sulphide, SnS, soluble in *yellow* ammonium sulphide, forming thiostannate, and in sodium hydroxide forming stannite and thiostannite, insoluble in ammonium carbonate:

$$SnS + (NH_4)_2S + S = (NH_4)_2SnS_3.$$

$$2SnS + 4OH' = SnS_2'' + SnO_2'' + 2H_2O.$$

Stannous sulphide is precipitated from the latter solution by hydrochloric acid, while the former yields yellow stannic sulphide, SnS_2.

$$SnS_2'' + SnO_2'' + 4H^{\cdot} = 2SnS + 2H_2O.$$

$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$

Stannous sulphide is also soluble in hot concentrated hydrochloric acid, in oxalic acid, and in tartaric acid.

2. **Mercuric chloride** is reduced by stannous salts, giving mercurous chloride, and finally mercury (**303**, 6).

3. **Sodium hydroxide** gives a white precipitate of stannous hydroxide, $Sn(OH)_2$, which dissolves in excess, forming sodium stannite, $Sn(ONa)_2$.

$Sn^{\cdot\cdot\cdot\cdot}$. Use stannic chloride, $SnCl_4$.

1. **Sulphuretted hydrogen** gives a yellow precipitate of stannic sulphide, SnS_2, soluble in ammonium sulphide, producing thiostannate, and in sodium hydroxide giving stannate and thiostannate. From these solutions hydrochloric acid precipitates the stannic sulphide. The sulphide is also soluble in hot, concentrated hydrochloric acid (distinction from arsenic).

2. **Sodium hydroxide** precipitates white stannic acid, H_2SnO_3, which is soluble in excess forming sodium stannate, Na_2SnO_3.

3. In test **309, 6**, for antimony, any tin which is present will be displaced from the solution by the zinc. It may then be detected by dissolving in hydrochloric acid and adding mercuric chloride. This gives a means of separating antimony from tin.

4. Spot Test. Soak a filter paper with a saturated aqueous solution of **cacotheline.** Reduce the tin solution with Zn and HCl and put a drop on the paper. A violet spot indicates tin. Titanous chloride is the only other metal chloride possessing a sufficiently powerful reducing action to reduce the cacotheline.

5. Add one drop of the tin solution reduced as above to 1 c.c. of a 0·01 per cent. aqueous solution of **diazine green** (Janus Green). A change of colour from blue to violet or red shows the presence of tin. Titanous chloride also gives the test.

SEPARATION OF THE COPPER GROUP

311. In the detection of the cations in this group, a division is first effected by the solution of the sulphides of arsenic, antimony and tin in yellow ammonium sulphide or sodium hydroxide. These three form a sub-group.

The detection of cations in the sub-group depends upon

(*a*) the reprecipitation of the sulphides from solution by hydrochloric acid,

(*b*) the solution of tin and antimony sulphides in conc. hydrochloric acid, arsenic sulphide being insoluble,

(*c*) the precipitation of antimony sulphide in presence of oxalic acid, tin remaining in solution,

(*d*) the reduction of the stannic to stannous ion and its detection by the reduction of mercuric chloride.

Another method of separation of the cations in the sub-group depends on the solubility of arsenic sulphide in ammonium carbonate, tin and antimony sulphides being insoluble.

The detection of the cations in the main group depends upon

(*a*) the solubility of the sulphides of lead, bismuth, copper and cadmium in nitric acid, mercuric sulphide being insoluble,

(*b*) the insolubility of bismuth hydroxide in ammonium hydroxide, copper and cadmium hydroxides being soluble,

(*c*) the precipitation of cadmium sulphide from potassium cadmicyanide and the non-precipitation of copper sulphide from the cuprocyanogen complex.

THE IRON GROUP

Cations whose hydroxides have a solubility product which is reached in presence of salts of weak bases, e.g. ammonium chloride.

312. **Iron.** DRY REACTIONS. 1. Heated on charcoal, iron compounds leave a black magnetic residue.

2. Heated in a borax bead in the oxidising flame, iron compounds form a red bead while hot, yellow on cooling. In the reducing flame the bead is bottle green.

REACTIONS IN SOLUTION. **$Fe^{\cdot\cdot}$.** Use ferrous sulphate or chloride.

1. To a portion of the solution add dilute hydrochloric acid and pass sulphuretted hydrogen. Boil off the sulphuretted hydrogen or take a fresh portion of the solution and add ammonium chloride and **ammonium hydroxide.** When the latter is added incomplete precipitation of ferrous hydroxide occurs. This precipitate is at first dirty white, changing to pale green,

grey, and finally brown, owing to oxidation to ferric hydroxide, $Fe(OH)_3$.

2. **Sodium hydroxide** causes similar changes.

3. **Ammonium sulphide** precipitates black ferrous sulphide, FeS, soluble in dilute acids.

4. **Sodium carbonate** gives a white precipitate of ferrous carbonate, $FeCO_3$, which rapidly oxidises.

5. **Potassium ferrocyanide** forms a white precipitate of potassium ferrous ferrocyanide, $K_2Fe[Fe(CN)_6]$, which rapidly turns blue through oxidation. Owing to this rapid oxidation the precipitate produced in the ordinary way is never white.

$$K_4Fe(CN)_6 + FeSO_4 = K_2Fe[Fe(CN)_6] + K_2SO_4.$$

6. **Potassium ferricyanide** forms a deep blue precipitate known as Turnbull's blue, identical in composition with Prussian blue (see **Fe‴**, 5). As the ferricyanide gives only a slight brown colour with ferric salts, it is used as an external indicator in the volumetric estimation of ferrous salts with dichromate (445).

Fe‴. Use ferric chloride, $FeCl_3$. 1. To a portion of the solution add hydrochloric acid and then pass sulphuretted hydrogen. Note the change in colour and the precipitate of sulphur. The ferric ion has been reduced to ferrous ion

$$2Fe''' + S'' \rightarrow 2Fe'' + S.$$

Boil off the sulphuretted hydrogen, add two or three drops of concentrated nitric acid, boil and add ammonium chloride and **ammonium hydroxide.** A brown precipitate of ferric hydroxide is obtained, the nitric acid having reoxidised the ferrous ion to ferric

$$6Fe'' + 8H' + 2NO_3' \rightarrow 6Fe''' + 4H_2O + 2NO.$$

In analytical work ferrous salts must always be oxidised to ferric, as the former are not completely precipitated by ammonium hydroxide.

Ferric hydroxide is soluble in hydrochloric acid, insoluble in sodium hydroxide. When strongly heated it leaves the oxide Fe_2O_3, which is unaffected by fusion with fusion mixture and potassium nitrate.

2. **Sodium hydroxide** precipitates ferric hydroxide, insoluble in excess of the reagent.

3. **Sodium carbonate** produces the same precipitate with evolution of carbon dioxide.

$$2Fe''' + 3CO_3'' + 3H_2O \rightarrow 2Fe(OH)_3 + 3CO_2.$$

4. **Ammonium sulphide** gives a black precipitate of ferric sulphide, Fe_2S_3, decomposed by dilute HCl into ferrous chloride and sulphur :

$$2Fe''' + 3S'' \rightarrow Fe_2S_3.$$

$$Fe_2S_3 + 4H^{\cdot} \rightarrow 2Fe'' + 2H_2S + S.$$

5. **Potassium ferrocyanide** precipitates deep blue ferric ferrocyanide (Prussian blue), $Fe_4[Fe(CN)_6]_3$, insoluble in hydrochloric acid but decomposed by caustic alkalis,

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 4Fe(OH)_3 + 3K_4Fe(CN)_6.$$

6. **Potassium ferricyanide** forms no precipitate, but the solution turns brown (compare ferrous and see use as indicator).

7. **Potassium thiocyanate** gives a blood-red coloration, due to the soluble ferric thiocyanate $Fe(SCN)_3$. This is a very delicate test for iron (see par. 66).

8. **Sodium phosphate** precipitates pale buff coloured ferric phosphate, $FePO_4$, which is soluble in mineral acids, but insoluble in acetic acid or ammonia.

Ferrous ions are easily oxidised (chlorine or nitric acid being generally used) to ferric ions, and ferric ions are easily reduced to ferrous.

$$6Fe'' + 8H^{\cdot} + 2NO_3' \rightarrow 6Fe''' + 4H_2O + 2NO.$$

$$2Fe''' + Sn'' \rightarrow 2Fe'' + Sn''''.$$

313. Chromium. Dry Reactions. 1. Heated on charcoal, chromium compounds leave a dark green residue.

2. Heated on platinum or porcelain with fusion mixture and a little nitre, a yellow mass of potassium and sodium chromates is obtained.

3. Heated in a borax bead, an emerald green bead is formed in either flame ($Cr_2O_3 . B_2O_3$).

REACTIONS IN SOLUTION. $Cr^{\cdots}$. Use chrome alum, or chromium sulphate.

1. As with iron, add hydrochloric acid, then sulphuretted hydrogen (no change), boil off the latter and add ammonium chloride and **ammonium hydroxide.** A bluish-green precipitate of chromic hydroxide, $Cr(OH)_3$, is formed, slightly soluble in excess, giving a lilac-coloured liquid containing complex chrome-ammine cations, from which the chromium hydroxide is completely precipitated by boiling. Chromium hydroxide is soluble in dilute acids.

2. **Sodium hydroxide** gives the same precipitate, which readily dissolves in excess to a bright green solution of sodium chromite $Cr(ONa)_3$. The hydroxide begins at once to separate from this solution when boiled, but for complete precipitation long boiling is required.

3. **Ammonium sulphide** produces the same precipitate.

$$2Cr^{\cdots} + 3S'' + 6H_2O \rightarrow 2Cr(OH)_3 + 3H_2S.$$

4. **Sodium carbonate** gives a precipitate of hydroxide and carbonate, which forms pure hydroxide on boiling, evolving CO_2.

$$2Cr^{\cdots} + 3CO_3'' + 3H_2O \rightarrow 2Cr(OH)_3 + 3CO_2.$$

5. **Sodium phosphate** precipitates pale green chromium phosphate, $CrPO_4 . 3H_2O$, soluble in mineral acids, insoluble in acetic acid or ammonia.

OXIDATION OF CHROMIUM COMPOUNDS

Chromium compounds are easily oxidised to chromates, as in the dry reaction (2) or as follows :

1. Add **sodium peroxide** to a cold solution of a chromic salt, and boil till effervescence ceases. Sodium chromate is formed.

$$2Cr^{\cdots} + 3Na_2O_2 + 4OH' \rightarrow 2CrO_4'' + 6Na^{\cdot} + 2H_2O.$$

2. **Sodium hypochlorite,** or sodium hydroxide and chlorine water or bromine water oxidise chromic salts.

$$2Cr^{\cdots} + 3OCl' + 10OH' \rightarrow 2CrO_4'' + 3Cl' + 5H_2O.$$

REACTIONS OF CHROMATES

CrO_4''. 1. **Sulphuretted hydrogen** in presence of an acid reduces the chromate to a chromic salt, the colour changing to green, and sulphur being precipitated.

$$Cr_2O_7'' + 3S'' + 14H^{\cdot} \rightarrow 2Cr^{\cdot\cdot\cdot} + 3S + 7H_2O.$$

2. **Sulphurous acid** also reduces chromates to green chromic salts, but no sulphur is precipitated ; sulphite anion is oxidised to sulphate.

$$Cr_2O_7'' + 3SO_3'' + 8H^{\cdot} \rightarrow 2Cr^{\cdot\cdot\cdot} + 3SO_4'' + 4H_2O.$$

3. **Silver nitrate** in neutral solutions forms a red precipitate of silver chromate, soluble in nitric acid.

4. **Lead nitrate** gives a yellow precipitate of lead chromate.

5. **Barium chloride** precipitates yellow barium chromate, soluble in hydrochloric acid, insoluble in acetic acid.

6. **Mercurous nitrate** produces a dark-red precipitate of mercurous chromate (501 C).

7. A few drops of a 1 per cent. solution of **diphenylamine** in sulphuric acid, added to a solution of a chromate or dichromate, causes an intense coloration of phenylene blue (see volumetric work, par. 445).

Chromates are easily reduced to chromic salts, and therefore chromates and chromic acid are powerful oxidising agents (94).

DISTINCTION BETWEEN CHROMATES AND DICHROMATES

Chromates are converted to dichromates on addition of acid, the colour changing from yellow to orange. Dichromates are changed to chromates by alkalis.

Chromates are neutral to litmus, while dichromates are acid. Solutions of dichromate decompose carbonates, carbon dioxide being evolved.

DETECTION OF A CHROMIUM SALT AND CHROMATE TOGETHER

Boil a little of the substance with sodium carbonate solution and filter. The residue will contain the chromium of the chromium

salt as hydroxide. A yellow filtrate shows the presence of chromate or dichromate. Confirm in the well-washed precipitate by the borax bead test and in the yellow filtrate by acidifying with acetic acid and adding lead acetate.

314. Aluminium. Dry Reaction. 1. Heated on charcoal, aluminium compounds leave white aluminium oxide, Al_2O_3, which when moistened with cobalt nitrate and reheated gives a blue mass of cobalt aluminate. (Silica and silicates, phosphates and borates, give a blue mass, but require to be fused.)

Reactions in Solution. $Al^{...}$. Use alum, or aluminium sulphate.

1. Add hydrochloric acid, etc., as before, then ammonium chloride and **ammonium hydroxide.** A white precipitate of aluminium hydroxide, $Al(OH)_3$, is produced, soluble in a large excess of the reagent, but completely reprecipitated on boiling, and insoluble in ammonium salts. The precipitate is also soluble in dilute acids.

2. **Sodium hydroxide** gives the same precipitate, readily soluble in excess, forming sodium aluminate, Na_3AlO_3, which is decomposed by ammonium chloride, the precipitation being complete on boiling. Sodium aluminate is also decomposed by dilute acids.

3. **Ammonium sulphide** forms the same precipitate, with evolution of sulphuretted hydrogen (see chromium).

4. **Sodium carbonate** produces a precipitate of hydroxide and carbonate, which gives pure hydroxide on boiling, as do the iron and chromium precipitates.

5. **Sodium phosphate** precipitates white aluminium phosphate, $AlPO_4$, soluble in mineral acids, but insoluble in acetic acid or ammonia.

6. To a slightly acid solution of an aluminium salt add a few c.c. of a dilute solution of ammonium acetate and an equal volume of a 0·1 per cent. aqueous solution of **aluminon** (ammonium aurin tricarboxylate). Make the solution just alkaline with ammonia. A bright red precipitate is produced. The test can be made with the precipitate of aluminium hydroxide obtained in the separation of the iron group.

7. SPOT TEST. $Al^{...}$ forms a red lake with alizarin. Fe, Cr, Mn, Th, U also form lakes, and to detect aluminium in the presence of these proceed as follows :

Soak a filter paper in potassium ferrocyanide and dry it. Add a drop of the neutral or slightly acid solution to be tested. The interfering metals are pptd. as ferrocyanides, but the aluminium spreads beyond and may be spread further by putting one drop of water in the centre of the ring. Now put a drop of an alcoholic solution of alizarin on the paper so that it spreads to the damp outer ring of the original spot. Expose the paper to ammonia and dry. A red zone will appear at the junction of the two spots if aluminium be present.

In the absence of the other metals an untreated filter paper may be used.

SEPARATION OF THE IRON GROUP

315. The detection and separation of the cations of the iron group depend upon

(*a*) The solubility of the hydroxides in hydrochloric acid.

(*b*) The addition of a slight excess of sodium peroxide which precipitates ferric hydroxide, precipitates chromium hydroxide and oxidises it to a soluble chromate, and precipitates and redissolves aluminium hydroxide.

Any manganese precipitated as Mn_2O_3 in the iron group is oxidised by sodium peroxide to manganese dioxide, MnO_2.

THE ZINC GROUP

Cations whose sulphides are precipitated in alkaline but not in acid solutions.

316. Zinc. DRY REACTIONS. 1. Heated in a bulb tube, most zinc compounds leave a residue of oxide, which is yellow when hot and white when cold.

2. Heated on charcoal with a little sodium carbonate, zinc compounds are reduced to the metal, which is volatile and easily oxidised. No bead is formed, but an incrustation of oxide appears

on the charcoal. When moistened with solution of cobalt nitrate and again heated, the residue becomes green (Rinmann's green, $CoZnO_2$).

REACTIONS IN SOLUTION. **$Zn^{..}$**. Use zinc sulphate, or chloride. To a portion of this solution add dilute hydrochloric acid, then sulphuretted hydrogen; next boil off the latter or take a fresh portion of the solution and add ammonium chloride and ammonia. Note the results and consider their utility. Repeat this procedure with the other ions of the group.

1. **Ammonium sulphide,** or H_2S in the alkaline solution, gives a white precipitate of zinc sulphide, ZnS, insoluble in alkalis or in acetic acid, soluble in mineral acids (see **93**).

2. **Ammonium hydroxide** gives a precipitate of zinc hydroxide. The precipitation is incomplete owing to the formation of complex zinc-ammonia ions in the solution:

$$Zn(OH)_2 + 6NH_3 \rightarrow [Zn(NH_3)_6]^{..} + 2OH'.$$

3. **Sodium hydroxide** precipitates white zinc hydroxide, $Zn(OH)_2$, soluble in excess, forming an alkaline zincate, $Zn(ONa)_2$. Sulphuretted hydrogen precipitates the zinc from this completely as sulphide.

4. **Sodium carbonate** produces a white precipitate of basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2$. Some carbon dioxide is liberated. This precipitate is also obtained with ammonium carbonate, but is soluble in excess and in other ammonium salts.

5. **Potassium cyanide** gives a white precipitate of zinc cyanide, soluble in excess, forming the complex cyanide, $K_2Zn(CN)_4$. This is decomposed by acids or by H_2S:

$$Zn(CN)_4'' + S'' \rightarrow ZnS + 4CN'.$$

6. **Acridine hydrochloride** in presence of ammonium thiocyanate produces with salts of zinc, iron and cobalt characteristic crystals of the double thiocyanates of the metal and acridine.

MICROSCOPE TEST. Place one drop of the solution to be tested on a microscope slide, add one drop of a one per cent. solution of acridine hydrochloride and a drop of one per cent. ammonium thiocyanate. Zinc forms square yellow plates, cobalt gives similarly shaped green crystals, and the iron salt is red.

317. Manganese. DRY REACTIONS. 1. All manganese compounds, heated with three parts of fusion mixture and a little nitre, on platinum or porcelain, produce a dark blue-green mass of alkaline manganate, Na_2MnO_4. If this is dissolved in water and the solution acidified with sulphuric acid, the colour changes to pink, owing to the formation of permanganate, $NaMnO_4$ (170).

2. The borax or microcosmic bead is coloured violet to amethyst in the oxidising flame ($Mn_2O_3 . B_2O_3$), but is colourless in the reducing flame ($MnO . B_2O_3$).

REACTIONS IN SOLUTION. **$Mn^{..}$.** Use manganous chloride or sulphate. Test with hydrochloric acid, etc., as directed under zinc.

1. **Ammonium sulphide** gives a pale yellow-pink precipitate of hydrated manganous sulphide, MnS, insoluble in alkalis, soluble in acetic acid or mineral acids.

2. **Sodium hydroxide** precipitates the white hydroxide, $Mn(OH)_2$, insoluble in excess, soluble in ammonium chloride. The precipitate rapidly turns brown through oxidation to hydrated sesquioxide, $Mn_2O_3 . H_2O$.

3. **Ammonium hydroxide** gives the same precipitate in absence of ammonium salts. In presence of ammonium chloride no precipitate is obtained, but by passing air through the warm solution the manganese may be completely precipitated as sesquioxide, $Mn_2O_3 . H_2O$. For this reason it is difficult to separate iron and manganese by means of ammonium chloride and hydroxide.

4. **Sodium peroxide**, sodium hypochlorite, or bromine water, added to the alkaline solution of manganous salts, oxidises the manganese to higher oxides, Mn_2O_3 or MnO_2, which are precipitated.

5. **Sodium carbonate** precipitates white manganous carbonate, $MnCO_3$, insoluble in excess, soluble in ammonium chloride. It oxidises in air to brown manganic hydroxide.

6. **Permanganic acid reaction.** Place some lead peroxide, or red lead, in a test-tube, add dilute nitric acid and a solution of manganous salt (except haloid salts) and warm gently. Allow the lead peroxide to settle. The liquid has now a rose-pink colour, due to permanganic acid.

7. SPOT TEST. See **Benzidine test, 301, 8.**

Permanganates. 1. **Heated alone,** these decompose into oxides of the metals and free oxygen, with some manganate.

$$2KMnO_4 = K_2O + 2MnO_2 + 3O.$$

2. Heated with **hydrochloric acid,** chlorides are produced, and free chlorine equivalent to the available oxygen.

$$2MnO_4' + 10Cl' + 16H^{\cdot} \rightarrow 2Mn^{\cdot\cdot} + 5Cl_2 + 8H_2O.$$

3. **All permanganates** dissolve in water, giving purple-red solutions. They are powerful oxidising agents, stable in the cold and in absence of easily oxidisable substances, but immediately reduced (decolorised) by sulphurous acid, sulphuretted hydrogen, ferrous salts, oxalic acid, etc.

4. **Hydrogen peroxide** and permanganates acidified with sulphuric acid immediately destroy each other when mixed, evolving oxygen in equal amounts. This reaction is employed for the estimation of peroxides and of permanganates (438–42, 558–9).

$$2MnO_4' + 5H_2O_2 + 6H^{\cdot} \rightarrow 2Mn^{\cdot\cdot} + 8H_2O + 5O_2.$$

318. Nickel. DRY REACTIONS. 1. Heated on charcoal with fusion mixture, metallic nickel is obtained as a grey magnetic powder.

2. The borax bead is coloured red-brown in the oxidising flame ($NiO \cdot B_2O_3$), and in the reducing flame colourless but slightly opaque from metallic nickel.

REACTIONS IN SOLUTION. **$Ni^{\cdot\cdot}$.** Use nickel sulphate or other salt.

1. **Ammonium sulphide** forms a black precipitate of nickelous sulphide, NiS, slightly soluble in excess, insoluble in acetic acid, soluble with difficulty in hydrochloric acid, readily in nitric acid, aqua regia, or hydrochloric acid and potassium chlorate.

2. **Sodium hydroxide** precipitates apple-green nickelous hydroxide, $Ni(OH)_2$, insoluble in excess, soluble in ammonia or its salts. On ignition it leaves grey nickelous oxide, NiO.

3. **Ammonium hydroxide** precipitates a green basic salt, $Ni_2SO_4(OH)_2$, soluble in excess, forming a deep blue solution containing complex nickel-ammine ions, $[Ni(NH_3)_6]^{\cdot\cdot}$.

4. **Sodium carbonate** precipitates an apple-green basic carbonate of varying composition. The same is obtained with ammonium carbonate, but is soluble in excess.

5. **Potassium cyanide** produces a green precipitate of nickelous cyanide, $Ni(CN)_2$, soluble in excess of potassium cyanide, forming the complex cyanide $K_2Ni(CN)_4$. Sulphuretted hydrogen gives no precipitate from this solution, the nickel forming part of the complex anion, $Ni(CN)_4''$, but the compound is completely decomposed by boiling with hydrochloric acid.

6. To the above solution in potassium cyanide add **sodium hypochlorite,** or sodium hydroxide and bromine water, and warm gently. Black nickelic hydroxide is precipitated.

$$2Ni(CN)_4'' + OCl' + 4OH' + H_2O \rightarrow 2Ni(OH)_3 + 8CN' + Cl'.$$

This reaction may be employed to separate nickel from cobalt.

7. **Dimethylglyoxime** (1 per cent. alcoholic solution) gives a fine carmine precipitate of the nickel salt

$$[HO . N : (C . CH_3)_2 : NO]_2Ni,$$

which is used for the estimation of the metal (502, B). The precipitate is practically insoluble in water, acetic acid or ammonia, but soluble in mineral acids. Cobalt is not precipitated by this reagent.

SPOT TEST. The above reaction can be carried out as a spot test on filter paper or on a spotting tile.

319. **Cobalt.** DRY REACTIONS. 1. Heated on charcoal, cobalt compounds are reduced less easily than those of nickel, giving a grey, feebly magnetic powder.

2. The borax bead is coloured deep blue in both oxidising and reducing flames ($CoO . B_2O_3$).

REACTIONS IN SOLUTION. $Co^{..}$. Use cobaltous chloride or nitrate.

1. **Ammonium sulphide** precipitates black cobaltous sulphide, CoS, insoluble in excess or in dilute acids, soluble in aqua regia.

2. **Sodium hydroxide** precipitates a blue basic salt, which absorbs oxygen from air, changing to olive-green $Co(OH)_3$.

3. **Ammonium hydroxide** gives a slight precipitate of a similar basic salt, soluble in excess, forming a red-brown solution. This absorbs oxygen on standing, and becomes red in colour, owing to the formation of stable cobalti-ammines.

4. **Potassium cyanide** gives a light brown precipitate of cobaltous cyanide, $Co(CN)_2$, soluble in excess, with formation of the complex cyanide $K_4Co(CN)_6$. Dilute acids reprecipitate cobaltous cyanide.

This substance is very readily oxidised to potassium cobalticyanide, the change taking place even on boiling with water alone, but more readily in presence of a little free hydrocyanic acid ; hydrogen is evolved in the absence of air ;

$$2K_4Co(CN)_6 + 2H_2O = K_3Co(CN)_6 + 2KOH + H_2,$$

or
$$2Co(CN)_6'''' + O + H_2O \rightarrow 2Co(CN)_6''' + 2OH'.$$

This cobaltic cyanide remains in solution as the complex potassium cobalticyanide, from which oxidising agents (NaOCl) give no precipitate.

5. To a concentrated solution of a cobalt salt, add sodium nitrite and acetic acid, and warm till brown fumes cease. Then add potassium nitrate and shake well or allow to stand. A bright yellow precipitate of a **cobaltinitrite**, $K_4Co(NO_2)_6$ or $K_2Na_2Co(NO_2)_6$, is obtained.

6. **Acridine hydrochloride.** MICROSCOPE TEST. (See 316, 6.)

7. **Ammonium thiocyanate** forms with cobaltous salts the beautiful blue double thiocyanate, $(NH_4)_2[Co(SCN)_4]$, soluble in amyl alcohol or in a mixture of equal volumes of this with ether. The blue compound is hydrolysed by water, the colour being replaced by the pink colour of the cobalt salt. The test is a very delicate one, but it is obscured by iron, which forms $Fe(SCN)_3$, also soluble in amyl alcohol. Nickel does not interfere with the test.

8. **α-Nitroso-β-naphthol** forms, in neutral or slightly acid solutions, a bulky red precipitate of cobalti-nitroso-β-naphthol, $Co[C_{10}H_6(NO)O]_3$. The test is a delicate one, and may be used also for the detection and estimation of cobalt in presence of nickel. It is best applied in the group separation to the solution

containing only nickel and cobalt (361). It may be used as a spot test on filter paper.

When Fe or Cu is present the method must be modified. To 2 c.c. of a slightly acid solution of the substance to be tested, add 1 g. of $NaC_2H_3O_2$ and 2 c.c. of 0·5 per cent. solution of nitroso-R-salt (the 3 : 6-disulphonic acid salt of the above). Boil the mixture, add 1 c.c. of conc. HNO_3 and boil for one minute. Cobalt gives a permanent red colour.

SEPARATION OF THE ZINC GROUP

320. The detection and separation of the cations in this group depend on :

(*a*) The solubility of zinc and manganous sulphides in dilute hydrochloric acid, those of nickel and cobalt being insoluble.

(*b*) The precipitation of zinc and manganous hydroxides by sodium hydroxide, the zinc compound alone being soluble in excess.

(*c*) The borax bead colour test for nickel and cobalt, followed by the precipitation of nickel as dimethylglyoxime salt, and of cobalt as a cobaltinitrite ; or by the formation of its soluble red compound with nitroso-β-naphthol.

THE BARIUM GROUP

Cations whose carbonates have a low solubility product.

321. **Barium.** Dry Reaction. Barium compounds give a persistent green colour to the Bunsen flame, especially when moistened with hydrochloric acid.

Reactions in Solution. $Ba^{\cdot\cdot}$. Use barium chloride.

Test small portions of the solutions of barium, strontium and calcium with the group reagents for the foregoing groups, namely (i) hydrochloric acid, (ii) hydrochloric acid and sulphuretted hydrogen, (iii) ammonium chloride and ammonia, and (iv) ammonium sulphide. Explain the results obtained.

It should be noted that concentrated HCl and HNO_3 cause

precipitation of $BaCl_2$ and $Ba(NO_3)_2$ respectively from aqueous solutions of these salts, as a result of the common ion effect. The salts dissolve again on dilution.

1. **Ammonium carbonate** gives a heavy white precipitate of barium carbonate, $BaCO_3$, decomposed by acetic acid, and slightly soluble in ammonium chloride, especially on warming.

2. **Sulphuric acid** or a soluble sulphate ($CaSO_4$) precipitates heavy white barium sulphate, $BaSO_4$, insoluble in dilute acids, slightly soluble in concentrated HCl.

3. **Potassium chromate** produces a lemon-yellow precipitate of barium chromate, $BaCrO_4$, soluble in mineral acids, practically insoluble in acetic acid.

4. **Ammonium oxalate** precipitates white barium oxalate, BaC_2O_4, soluble in mineral acids or in oxalic or acetic acids when freshly precipitated.

5. **Sodium phosphate** in neutral or alkaline solutions of barium salts forms the secondary phosphate :

$$Ba^{\cdot\cdot} + HPO_4'' \rightarrow BaHPO_4.$$

Ammonia converts this partially or completely into the tertiary salt :

$$HPO_4'' + OH' \rightarrow PO_4''' + H_2O,$$

$$2PO_4''' + 3Ba^{\cdot\cdot} \rightarrow Ba_3(PO_4)_2.$$

6. **Rhodizonic acid**, $H_2C_6O_6$, or its sodium salt, in one per cent. aqueous solution, forms reddish brown compounds with barium and strontium salts. The reaction may be used as a spot test. On adding dilute HCl the strontium compound dissolves ; the barium spot becomes a brilliant red.

322. **Strontium.** DRY REACTION. Strontium compounds impart an intense crimson colour to the Bunsen flame.

REACTIONS IN SOLUTION. $Sr^{\cdot\cdot}$. Use strontium chloride.

1. **Ammonium carbonate** gives a white precipitate of strontium carbonate, $SrCO_3$, decomposed by acetic acid.

2. **Sulphuric acid** produces a white precipitate of strontium sulphate, $SrSO_4$. The precipitation is slow from dilute solutions, and is accelerated by adding ammonium sulphate.

3. **Potassium chromate** precipitates yellow strontium chromate, $SrCrO_4$, from solutions which are not too dilute. The chromate is soluble in acetic or mineral acids.

4. **Ammonium oxalate** gives a white precipitate of strontium oxalate, SrC_2O_4, less soluble than barium oxalate, decomposed by mineral acids.

5. **Sodium phosphate** precipitates $SrHPO_4$, which behaves like $BaHPO_4$.

323. Calcium. DRY REACTION. The Bunsen flame is coloured yellowish red by most calcium compounds, especially when moistened with hydrochloric acid.

REACTIONS IN SOLUTION. $Ca^{\cdot\cdot}$. Use calcium chloride.

1. **Ammonium carbonate** precipitates white, amorphous calcium carbonate, $CaCO_3$, which becomes crystalline on standing. This is soluble in acetic acid and slightly soluble in ammonium chloride, especially on boiling.

2. **Sulphuric acid** gives from concentrated solutions of calcium salts a white precipitate of calcium sulphate, $CaSO_4$, soluble in ammonium sulphate solution, or in acids.

3. **Potassium chromate** causes no precipitation, calcium chromate being soluble in water.

4. **Ammonium oxalate** produces even from very dilute solutions a white crystalline precipitate of calcium oxalate, $CaC_2O_4 . H_2O$, soluble in mineral acids, insoluble in acetic acid or ammonia.

5. **Sodium phosphate** precipitates white, flocculent $CaHPO_4$ from neutral solutions. Ammonia converts this completely into tri-calcic phosphate, $Ca_3(PO_4)_2$. All the phosphates of this group are soluble in dilute HCl or HNO_3, but $Ca_3(PO_4)_2$ is not appreciably soluble in acetic acid (360).

SEPARATION OF THE BARIUM GROUP

324. The separation and detection of these cations is based on the facts that barium chromate is insoluble in acetic acid, the others being soluble, and that strontium sulphate is insoluble in ammonium sulphate solution, while calcium sulphate is soluble.

THE SODIUM GROUP

This group comprises potassium, sodium, lithium and magnesium, and the complex cation ammonium, NH_4, which are not precipitated by any previous group reagent. The rare elements rubidium and caesium also appear in this group.

325. **Potassium.** DRY REACTION. Potassium compounds colour the Bunsen flame violet. This cannot be detected in presence of sodium, unless a cobalt glass or permanganate or indigo prism be used, which does not transmit the yellow sodium light.

REACTIONS IN SOLUTION. $K^{\cdot}$. Use potassium chloride.

1. **Platinic chloride** gives a heavy, golden-yellow crystalline precipitate of potassium platinichloride, K_2PtCl_6, slightly soluble in water, insoluble in acids or in alcohol. If no precipitate is obtained, evaporate to a small bulk and add an equal volume of alcohol. See also the estimation of potassium (**521, B**).

2. **Tartaric acid** precipitates white crystalline potassium bitartrate, $KHC_4H_4O_6$ from concentrated solutions, especially on shaking.

3. **Sodium cobaltinitrite** forms with neutral potassium salts a yellow precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$. Mixed sodium-potassium cobaltinitrites may also come down. Ammonium salts give a similar precipitate, and must be removed before applying the test (**363**).

326. **Sodium.** DRY REACTION. An intense golden-yellow colour is imparted to the Bunsen flame, the light appearing through the spectroscope as a bright double line, coinciding with the solar D line. The reaction is a very delicate one, and the coloration should be strong and persistent.

REACTION IN SOLUTION. $Na^{\cdot}$. Use sodium chloride. **Potassium antimonate,** $K_2H_2Sb_2O_7$, precipitates white $Na_2H_2Sb_2O_7$ from solutions of sodium salts.

327. **Lithium.** DRY REACTION. The Bunsen flame is coloured crimson by lithium compounds, the spectrum containing two lines, a bright crimson and a feebler orange line.

REACTIONS IN SOLUTION. $Li^{\cdot}$. Use lithium chloride. Platinum chloride or tartaric acid gives no precipitate.

1. **Sodium phosphate** gives, on boiling, a white precipitate of lithium phosphate, $2Li_3PO_4 . H_2O$, especially in presence of sodium hydroxide. The precipitate is soluble in hydrochloric acid or in ammonium salts.

2. **Alkali carbonates** precipitate from strong solutions white crystalline lithium carbonate, Li_2CO_3, insoluble in alcohol, decomposed by acids.

3. **Ammonium fluoride** in presence of free ammonia slowly precipitates white gelatinous lithium fluoride, Li_2F_2.

328. Ammonium. DRY REACTION. When heated in a dry tube, ammonium salts volatilise either wholly (those with volatile acids) or partly (those with fixed acids, as phosphoric). In the former case a sublimate will form on the cold part of the tube. On adding a little soda lime and again heating, free ammonia is obtained.

REACTIONS IN SOLUTION. $NH_4^{\cdot}$. Use ammonium chloride.

1. **Platinic chloride** gives a heavy yellow crystalline precipitate of ammonium platinichloride $(NH_4)_2PtCl_6$, soluble in much water, insoluble in alcohol. On ignition, this compound leaves only spongy platinum,

$$3(NH_4)_2PtCl_6 \rightarrow 2N_2 + 2NH_3 + 18HCl + 3Pt,$$

and is thus distinguished from the similar potassium compound, which leaves potassium chloride and platinum (521, B).

2. All ammonium salts are decomposed when heated with **sodium hydroxide** solution, or ground with a little moistened soda lime, evolving free ammonia.

3. **Nessler's reagent** gives a brown precipitate of dimercur-ammonium iodide, or a yellow or brown coloration in solutions containing mere traces of ammonia, such as occur in waters. It is too sensitive for ordinary use.

$$2K_2HgI_4 + 4OH' + NH_4^{\cdot} \rightarrow NHg_2I . H_2O + 7I' + 4K^{\cdot} + 3H_2O.$$

329. Magnesium. DRY REACTION. Magnesium compounds leave a white residue on charcoal, which becomes incandescent.

If this is moistened with cobalt nitrate and again heated, it becomes pink. This reaction, however, is only reliable in absence of other oxides.

REACTIONS IN SOLUTION. $Mg^{\cdot\cdot}$. Use magnesium sulphate.

1. **Ammonium hydroxide** produces a partial precipitate of magnesium hydroxide, $Mg(OH)_2$, soluble in ammonium chloride. Ammonium salts completely prevent this precipitation (92).

2. **Potassium,** sodium, calcium or barium **hydroxides** precipitate magnesium hydroxide almost completely. It is almost insoluble in cold or hot water, readily soluble in dilute acids.

3. **Sodium phosphate** gives a white precipitate of magnesium hydrogen phosphate, $MgHPO_4$. In presence of ammonia, magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, is obtained as a white crystalline precipitate, practically insoluble in dilute ammonium hydroxide, soluble in mineral acids or in acetic acid. From very dilute solutions the precipitate forms very slowly.

$$Mg^{\cdot\cdot} + NH_4^{\cdot} + PO_4''' + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O.$$

When ignited the precipitate is decomposed into magnesium pyrophosphate, with loss of ammonia and water (508, A).

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

4. **Sodium carbonate** precipitates basic carbonates, such as $3MgCO_3 \cdot Mg(OH)_2$, the composition of which varies with concentration and temperature. Sodium **bicarbonate** causes no precipitation.

DETECTION OF THE METALS OF THE SODIUM GROUP

330. In this group the flame coloration is a reliable test for sodium, potassium and lithium, especially if examined by means of a spectroscope. Potassium is confirmed by the reaction with platinic chloride or sodium cobaltinitrite.

Ammonium compounds are detected in the original substance.

The only separation necessary is that of magnesium from lithium. This is effected by precipitating the magnesium in cold solution with sodium phosphate and ammonia, and the lithium by boiling the filtrate with sodium hydroxide

REACTIONS OF THE ANIONS

331. Hydrochloric acid. REACTIONS. Use sodium chloride.

1. Warmed with concentrated **sulphuric acid,** chlorides liberate hydrogen chloride, which is recognised by its smell and by the fumes in moist air.

2. Warmed with concentrated **sulphuric acid** and **manganese dioxide,** chlorine is liberated, recognised by its smell, and its bleaching action on litmus paper.

3. Warmed with concentrated **sulphuric acid** and **potassium dichromate,** a red vapour of chromyl chloride, CrO_2Cl_2, is given off (see chromyl chloride, **136**).

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 = 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O.$$

The vapour, when poured into a test-tube containing water, gives a yellow solution of chromic acid and hydrochloric acid. If sodium hydroxide be used instead of water a yellow solution of chromate and chloride will be produced.

$$CrO_2Cl_2 + 4OH' = CrO_4'' + 2Cl' + 2H_2O.$$

The chromate may be identified by acidifying with acetic acid and adding lead acetate. (Compare the action of bromine on sodium hydroxide.) This gives a means of detecting chlorides in presence of bromides.

4. REACTION IN SOLUTION. **Cl′. Silver nitrate** gives a white precipitate of silver chloride, AgCl, readily soluble in ammonium hydroxide, but insoluble in nitric acid (see **302, 1**).

332. Hydrobromic acid. REACTIONS. Use potassium bromide.

1. Warmed with concentrated **sulphuric acid,** bromides give hydrobromic acid and bromine, the latter owing to oxidation of part of the hydrobromic acid by the sulphuric acid.

$$2HBr + H_2SO_4 \rightleftharpoons 2H_2O + SO_2 + Br_2.$$

2. With sulphuric acid and **manganese dioxide,** bromine is liberated. Dichromate and sulphuric acid also liberate bromine; no bromine compound is formed corresponding to CrO_2Cl_2.

REACTIONS IN SOLUTION. **Br′.**

3. **Silver nitrate** gives a pale yellow precipitate of silver bromide, AgBr, soluble with difficulty in ammonium hydroxide, and insoluble in nitric acid.

4. **Chlorine water** (but not sodium hypochlorite or nitrous acid) added to a solution of a bromide liberates bromine, and on shaking with carbon disulphide or chloroform a brown layer is formed. Excess of chlorine water *gradually* oxidises the bromine to bromic acid, $HBrO_3$.

333. Hydriodic acid. REACTIONS. Use potassium iodide.

1. Warmed with concentrated **sulphuric acid,** iodides give a small quantity of hydriodic acid, together with much iodine. The smell of sulphuretted hydrogen may be detected.

$$2KI + H_2SO_4 = K_2SO_4 + 2HI.$$
$$8HI + H_2SO_4 = 4H_2O + H_2S + 4I_2.$$

2. Warmed with concentrated sulphuric acid and **manganese dioxide,** iodine is liberated.

REACTIONS IN SOLUTION. **I′.**

3. **Silver nitrate** gives a pale yellow precipitate of silver iodide, AgI, insoluble in ammonium hydroxide or in nitric acid, but soluble in potassium cyanide or thiosulphate.

4. **Chlorine water,** sodium hypochlorite or nitrous acid liberates iodine from iodides, and on shaking with carbon disulphide, a violet layer is obtained. The chlorine water must be added drop by drop, as the iodine liberated is very readily converted into iodic acid.

$$I + 3H_2O + 5Cl = HIO_3 + 5HCl.$$

If bromine and iodine are liberated together in this manner and shaken with carbon disulphide, the iodine colour masks that of the bromine, but by careful addition of chlorine water the colour of the iodine disappears and that of bromine is left.

5. **Copper sulphate** in presence of sulphurous acid, thiosulphate or ferrous sulphate, gives a white precipitate of cuprous iodide, Cu_2I_2.

$$2CuSO_4 + 2KI + H_2SO_3 + H_2O = 2KHSO_4 + H_2SO_4 + Cu_2I_2.$$

By this means the iodide may be removed, and after boiling off the excess of sulphurous acid one part of the filtrate can be tested for bromide with chlorine water and carbon disulphide, and another part evaporated and tested by the chromyl chloride test for chloride.

To test for the halogens in presence of a cyanide, first remove the cyanide by boiling with dilute nitric acid, or with excess of sodium bicarbonate. Or precipitate with excess of $AgNO_3$ and ignite the precipitate. Silver cyanide is decomposed, the halides only fused (see 373).

6. **Starch paste** gives with free iodine a deep blue coloration.

334. **Hydrofluoric acid.** REACTIONS. Use sodium fluoride.

1. Warmed with concentrated **sulphuric acid,** fluorides liberate hydrofluoric acid, which will etch glass. Use a leaden dish for this experiment. If a test-tube is used a greasy appearance is often noticed in the tube.

2. Heated with concentrated **sulphuric acid** and **sand,** silicon tetrafluoride is produced (see preparation of silica, 177). On holding a moist glass rod near the mixture a deposit of silicic acid is formed on the rod.

REACTIONS IN SOLUTION. **F′.**

1. **Calcium** or barium **chloride** gives a white precipitate of fluoride, CaF_2 or BaF_2.

2. **Silver nitrate** gives no precipitate.

3. **Ferric chloride** added to a concentrated solution of an alkali fluoride precipitates a white complex fluoride corresponding in composition to cryolite, $Na_3(AlF_6)$. The aqueous solution of $Na_3(FeF_6)$ gives no colour with thiocyanate until acidified.

335. **Hypochlorous acid.** Use sodium hypochlorite, NaOCl, or bleaching powder, CaCl(OCl). The peculiar smell of hypochlorites is due to free hypochlorous acid, which is liberated by the action of atmospheric carbon dioxide.

$$NaOCl + CO_2 + H_2O = HOCl + NaHCO_3.$$

REACTIONS IN SOLUTION. **OCl'.** 1. When **heated** in solution, or in the dry state, hypochlorite is converted into chloride and chlorate :

$$3Ca(OCl)_2 = 2CaCl_2 + Ca(ClO_3)_2.$$

2. When the solution is heated with a little **cobalt oxide** (obtained by addition of cobalt nitrate solution), oxygen is evolved, and a chloride left :

$$Ca(OCl)_2 = CaCl_2 + O_2.$$

3. On adding dilute **hydrochloric acid,** chlorine is liberated, which may be detected by adding a few drops to a solution of potassium iodide and starch (distinction from chlorate).

$$OCl' + Cl' + 2H^{\cdot} \rightarrow H_2O + Cl_2.$$

4. The acidified solution has a powerful **bleaching action** on vegetable colours—litmus and indigo are decolorised. In alkaline solution also hypochlorites act as oxidising agents (distinction from chlorates). Ferrous hydroxide is rapidly changed to ferric hydroxide :

$$2Fe(OH)_2 + OCl' + H_2O \rightarrow 2Fe(OH)_3 + Cl'.$$

336. Chloric acid. Use potassium chlorate.

REACTIONS. All chlorates give off oxygen on heating, leaving chlorides. The oxygen contains traces of chlorine.

REACTIONS IN SOLUTION. **ClO_3'.** 1. Heated gently with concentrated **sulphuric acid,** chlorine peroxide, ClO_2, is liberated, a yellowish green, explosive gas. Use only one small crystal of chlorate :

$$3KClO_3 + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O..$$

2. Warmed with dilute **hydrochloric acid,** chlorine is obtained :

$$ClO_3' + 5Cl' + 6H^{\cdot} \rightarrow 3H_2O + 3Cl_2,$$

but **concentrated** hydrochloric acid yields a mixture of chlorine and chlorine peroxide :

$$2ClO_3' + 2Cl' + 4H^{\cdot} \rightarrow 2H_2O + Cl_2 + 2ClO_2.$$

Indigo solution is decolorised by this mixture.

3. **Ferrous salts** reduce chlorates to chlorides on warming in presence of dilute sulphuric acid :

$$ClO_3' + 6Fe'' + 6H^{\cdot} \rightarrow 6Fe''' + Cl' + 3H_2O.$$

Perchlorates are not reduced in this way.

337. Carbonic acid. DRY REACTIONS. Carbonates of the heavy metals liberate carbon dioxide when heated, leaving the oxide. The alkali carbonates fuse without decomposition.

Bicarbonates when heated alone, or when boiled in water, give off water and carbon dioxide, leaving carbonates (distinction between carbonates and bicarbonates).

REACTIONS IN SOLUTION. CO_3''. Use sodium carbonate, $Na_2CO_3 . 10H_2O$.

1. Dilute **hydrochloric acid** liberates carbon dioxide, which may be recognised by pouring the gas into lime-water. The latter is turned milky.

2. **Silver nitrate** forms a white precipitate of silver carbonate, soluble in dilute nitric acid or in ammonium hydroxide.

3. **Barium chloride** produces a white precipitate of barium carbonate, soluble in dilute hydrochloric acid.

4. **Potassium dichromate** liberates carbon dioxide from carbonates or bicarbonates, but does not liberate sulphur dioxide from sulphites. The dichromate is converted into chromate, with change of colour. (Compare **339, 5.**)

Bicarbonates give no precipitate with *cold* solutions of magnesium or calcium salts, but on warming the normal carbonate is precipitated.

338. Hydrosulphuric acid (sulphuretted hydrogen). REACTION. **Hydrochloric acid** decomposes all soluble and many insoluble sulphides, liberating H_2S, which blackens lead acetate paper. Concentrated H_2SO_4 decomposes all sulphides, most of the sulphur forming SO_2.

REACTIONS IN SOLUTION. S''. Use sodium sulphide, Na_2S.

1. **Silver nitrate** gives a black precipitate of silver sulphide, soluble in nitric acid. Solutions of other metallic salts, as those

of copper, cadmium or lead, may also be used, and sulphuretted hydrogen may be separated in this way from mixtures with carbon dioxide.

2. **Silver metal** (or lead or copper) is blackened by contact with a moist soluble sulphide or by hydrogen sulphide (Hepar's reaction) :

$$4Ag + 2S'' + 2H_2O + O_2(air) \rightarrow 2Ag_2S + 4OH'.$$

3. **Sodium nitroprusside,** $Na_2[Fe(CN)_5NO] \cdot 2H_2O$, gives an intense purple colour with small concentrations of sulphide ion, S''. Neutral or acid solutions of H_2S do not give the reaction.

4. **Lead acetate** solution containing excess of sodium hydroxide produces a black precipitate of PbS, or a dark coloration, with traces of S''. This is a very delicate test, used in colourimetric estimations of either the lead or the sulphide ion.

339. Sulphurous acid. DRY REACTION. Use sodium sulphite, $Na_2SO_3 \cdot 7H_2O$. Heated on charcoal, a sulphide is formed ; when the residue is placed on a silver coin and moistened with water, a black stain is produced. All sulphur compounds give this reaction, which merely indicates the presence of sulphur.

REACTIONS IN SOLUTION. SO_3''.

1. Dilute **hydrochloric acid** liberates sulphur dioxide, which is recognised by its smell, and by reduction of potassium dichromate solution on a strip of filter paper held in the mouth of the test-tube. Green chromium sulphate is produced.

2. **Barium chloride** gives with strong solutions a white precipitate of barium sulphite, soluble in hydrochloric acid.

3. **Silver nitrate** produces a white precipitate of silver sulphite, soluble in nitric acid, in ammonium hydroxide, and in excess of sodium sulphite to form sodium argentisulphite, $Na(AgSO_3)$. If this solution is boiled, the silver is precipitated :

$$2AgSO_3' \rightarrow 2Ag + SO_4'' + SO_2.$$

If water containing Ag_2SO_3 in suspension be boiled, half the metal is precipitated, the rest forming sulphate :

$$2Ag_2SO_3 \rightarrow 2Ag + Ag_2SO_4 + SO_2.$$

4. **Chlorine or bromine water** oxidises sulphites to sulphates, for which the solution may then be examined.

$$SO_3'' + Ba^{\cdot\cdot} + Br_2 + H_2O \rightarrow BaSO_4 + 2H^{\cdot} + 2Br'.$$

5. **Potassium dichromate** does not liberate sulphur dioxide from sulphites, but is itself reduced to green chromic sulphate (313). It may be used to separate sulphur dioxide and sulphuretted hydrogen from mixtures of these gases with carbon dioxide.

340. Sulphuric acid. DRY REACTION. Use sodium sulphate, $Na_2SO_4 . 10H_2O$. Heated on charcoal with fusion mixture, a sulphide is produced.

$$BaSO_4 + 2C + Na_2CO_3 = Na_2S + BaCO_3 + 2CO_2.$$

The product, placed on a silver coin and moistened, produces a brown stain.

REACTIONS IN SOLUTION. SO_4''.

1. **Barium chloride** gives a heavy white precipitate of barium sulphate, insoluble in acids.

2. **Silver nitrate** in concentrated solutions precipitates white crystalline Ag_2SO_4, soluble in 173 parts of water at room temperature.

3. **Lead acetate** forms a heavy white precipitate of $PbSO_4$, soluble with difficulty in concentrated HCl, soluble in ammonium acetate or tartrate (358).

341. Thiosulphuric acid. DRY REACTION. Use sodium thiosulphate, $Na_2S_2O_3 . 5H_2O$.

Heated on charcoal with fusion mixture, a sulphide is produced.

REACTIONS IN SOLUTION. S_2O_3''.

1. Dilute **hydrochloric acid** decomposes thiosulphates liberating sulphur dioxide and precipitating sulphur. (Compare sulphites.)

$$S_2O_3'' + 2H^{\cdot} \rightarrow H_2O + SO_2 + S.$$

2. **Barium chloride** gives no precipitate from dilute solutions.

3. **Silver nitrate** in excess gives a white precipitate of silver thiosulphate which on boiling turns yellow, brown, and finally

black (Ag_2S). The white precipitate dissolves in excess of the sodium salt, and when this solution is boiled it also throws out silver sulphide :

$$Ag_2(S_2O_3)_3'''' \rightarrow Ag_2S + S + SO_2 + SO_4'' + S_2O_3''.$$

4. **Cupric** and **ferric** salts are reduced to colourless cuprous and ferrous salts, which form soluble complexes, tetrathionate also being obtained :

$$2S_2O_3'' + 2Cu^{\bullet\bullet} \rightarrow 2Cu^{\bullet} + S_4O_6''.$$
$$2S_2O_3'' + 2Fe^{\bullet\bullet\bullet} \rightarrow 2Fe^{\bullet\bullet} + S_4O_6''.$$

The substance on boiling is decomposed with formation of the metallic sulphide :

$$Cu_2(S_2O_3)_2'' \rightarrow 2CuS + SO_4'' + SO_2.$$

5. **Iodine** solution and starch iodide are at once decolourised, the solution remaining neutral (see estimation, **449**).

$$2S_2O_3'' + I_2 \rightarrow S_4O_6'' + 2I'.$$

6. **Potassium cyanide,** on boiling with a thiosulphate, converts it into sulphite and forms thiocyanate :

$$S_2O_3'' + CN' \rightarrow SO_3'' + SCN'.$$

When the solution is acidified with HCl, $FeCl_3$ produces the deep red $Fe(SCN)_3$. Polysulphides on similar treatment also form thiocyanate.

DETECTION OF SULPHITE, THIOSULPHATE AND SULPHIDE TOGETHER

Test a little of the alkaline solution with sodium nitroprusside. If sulphide is shown to be present by the appearance of a red-violet colour, remove it by shaking with freshly precipitated $CdCO_3$. To the filtrate add a drop of phenolphthalein and pass CO_2 until the colour disappears. Test a few c.c. of this solution with fuchsin-malachite green solution (made by dissolving 0·05 g. each of fuchsin and malachite green separately in 200 c.c. of water and mixing three volumes of the first with one of the

second). Sulphite decolorises this solution : sulphide also does, and therefore it is first removed. Acidify another portion of the main solution with HCl and allow to stand. If thiosulphate is present, sulphur is precipitated, slowly from dilute solutions.

342. Nitrous acid. DRY REACTION. Use sodium nitrite, $NaNO_2$. Heated on charcoal, nitrites deflagrate.

REACTIONS IN SOLUTION. 1. **NO_2'.** Dilute **hydrochloric acid** liberates brown fumes of nitrogen peroxide, together with nitric oxide.

2. A crystal or a solution of **ferrous sulphate** is turned brown when added to a solution of a nitrite, owing to the formation of the compound $(FeSO_4)_2 . NO$.

3. **Potassium iodide** is decomposed by an acidified solution of a nitrite, liberating iodine, which gives a blue colour with starch.

$$2I' + 2NO_2' + 4H^{\cdot} \rightarrow I_2 + 2NO + 2H_2O.$$

4. Acidified **potassium permanganate** is decolorised, the nitrite being oxidised to nitrate (see estimation, 443).

$$2MnO_4' + 5NO_2' + 6H^{\cdot} \rightarrow 2Mn^{\cdot\cdot} + 5NO_3' + 3H_2O.$$

5. **Cobalt nitrate** added to a concentrated solution of potassium nitrite precipitates the sparingly soluble potassium cobaltinitrite, $K_3Co(NO_2)_6$.

6. **Ammonium chloride** decomposes nitrites on warming in dilute solution :

$$NH_4^{\cdot} + NO_2' \rightarrow N_2 + 2H_2O.$$

This reaction is employed to decompose nitrite before examining a solution for nitrate (343, 6).

7. **Urea** and **thiourea** decompose nitrous acid, that is, a nitrite acidified with acetic acid :

$$2HNO_2 + CO(NH_2)_2 \rightarrow 2N_2 + CO_2 + 3H_2O.$$

$$HNO_2 + CS(NH_2)_2 \rightarrow N_2 + HSCN + 2H_2O.$$

In the latter case $FeCl_3$ forms the deep red $Fe(SCN)_3$.

8. ***m*-Phenylenediamine** in dilute acid solution gives with acidified nitrite a precipitate of Bismarck brown, or a brown

coloration. The test is very sensitive, and is used for the colorimetric estimation of nitrite in water analysis.

343. Nitric acid. DRY REACTIONS. Use potassium nitrate, KNO_3.

1. Heated on charcoal, nitrates deflagrate.

2. Heated in a dry tube the nitrates of the heavy metals give off nitrogen peroxide and oxygen, and leave an oxide. The nitrates of the alkali metals on strongly heating give off oxygen and leave a nitrite, and finally an oxide.

REACTIONS IN SOLUTION. **NO_3'.** 3. Concentrated **sulphuric acid** added to a solution of a nitrate liberates nitric acid, and on the addition of copper, brown fumes are evolved.

4. If a solution of a nitrate is mixed with an equal bulk of **ferrous sulphate** solution, and concentrated **sulphuric acid** poured carefully down the tube, so forming a separate layer at the bottom, a brown coloration is formed at the junction of the layers. The brown substance has the composition $(FeSO_4)_2 . NO$, and is decomposed on warming, liberating nitric oxide. The brown colour is thus discharged. Iodides, bromides and nitrites interfere with this test.

$$3Fe^{\cdot\cdot} + NO_3' + 4H^{\cdot} \rightarrow 3Fe^{\cdot\cdot\cdot} + NO + 2H_2O.$$

5. Nitrates and nitrites are reduced to ammonia when boiled with sodium hydroxide solution and aluminium foil or Devarda's alloy (425).

DETECTION OF NITRATES IN PRESENCE OF BROMIDES, IODIDES AND NITRITES

6. Boil the substance with sodium hydroxide solution until all ammonium compounds, if present, are decomposed. Add a piece of aluminium foil and boil again ; nitrates and nitrites are completely reduced and evolution of ammonia now indicates the presence of one or both.

If nitrites are present, they must be removed before applying the above test, by boiling for a few minutes with ammonium chloride.

Chromic acid and permanganic acid. (See pars. 313 and 317.)

Phosphoric acids. Orthophosphoric acid, H_3PO_4.
Pyrophosphoric acid, $H_4P_2O_7$.
Metaphosphoric acid, HPO_3.

344. Orthophosphates. DRY REACTION. Use disodium phosphate, $Na_2HPO_4 . 12H_2O$.

Heated on charcoal, moistened with cobalt nitrate and reheated, phosphates give a blue mass on fusion.

REACTIONS IN SOLUTION. HPO_4''.

1. **Silver nitrate** produces a canary yellow precipitate of silver phosphate, Ag_3PO_4, soluble in nitric acid, dilute acetic acid or ammonium hydroxide.

$$2HPO_4'' + 3Ag^{\cdot} \rightarrow Ag_3PO_4 + H_2PO_4'.$$

2. **Barium chloride** gives a white precipitate of barium hydrogen phosphate, $BaHPO_4$, soluble in acetic acid. From ammoniacal solutions, however, the less soluble tertiary salt is precipitated :

$$2HPO_4'' + 3Ba^{\cdot\cdot} + 2NH_3 \rightarrow Ba_3(PO_4)_2 + 2NH_4^{\cdot}.$$

3. **Ammonium molybdate** when added in large excess to a solution of a phosphate in the presence of concentrated nitric acid produces a yellow precipitate of ammonium phosphomolybdate,

$$(NH_4)_3PO_4 . 12MoO_3,$$

either at once or on very gentle warming. (Cf. arsenates, 308, 5.) This precipitate is soluble in alkalis and in ammonia :

$$(NH_4)_3PO_4 . 12MoO_3 + 23OH' \rightarrow 3NH_4^{\cdot} + HPO_4'' + 12MoO_4'' + 11H_2O.$$

4. **Magnesia mixture** forms a white precipitate of magnesium ammonium phosphate, $MgNH_4PO_4 . 6H_2O$, soluble in acids, insoluble in ammonium hydroxide. (Cf. arsenates, 308, 4.)

$$HPO_4'' + Mg^{\cdot\cdot} + NH_3 \rightarrow MgNH_4PO_4.$$

5. **Ferric chloride** gives a yellowish white precipitate of ferric phosphate, $FePO_4$, soluble in excess of ferric chloride or in mineral acids, insoluble in acetic acid :

$$HPO_4'' + Fe^{\cdot\cdot\cdot} \rightleftharpoons FePO_4 + H^{\cdot}.$$

If the hydrogen ions produced in the reaction are removed (by adding sodium acetate) all the iron is precipitated.

Pyrophosphates give a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$, soluble in nitric acid and in ammonium hydroxide. Metaphosphates also give a white precipitate of silver metaphosphate, $AgPO_3$, similarly soluble.

Magnesia mixture precipitates pyrophosphates but not metaphosphates.

Metaphosphates in presence of acetic acid coagulate albumen.

Pyro- and meta-phosphates in cold solution very slowly pass into orthophosphates, but the change is greatly accelerated by boiling or by hydrogen ions. Tests for these phosphates should be made therefore in freshly prepared solutions.

Pyro- and meta-phosphates are converted into orthophosphates also on fusion with alkali carbonates. In this respect sodium metaphosphate, $NaPO_3$ or $(NaPO_3)_n$, prepared by the ignition of microcosmic salt (183), is useful for bead tests, as it unites with metallic oxides to form orthophosphates, many of which have characteristic colours. (Cf. borax, 347, 1.)

$$NaPO_3 + CoO \rightarrow CoNaPO_4.$$

345. **Phosphorous acid.** DRY REACTION. Use the sodium salt, Na_2HPO_3.

Phosphorous acid and phosphites when heated strongly give off phosphine, leaving a phosphate :

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

REACTIONS IN SOLUTION. HPO_3''.

1. **Silver nitrate** gives a white precipitate of silver phosphite, Ag_2HPO_3, which rapidly turns black owing to reduction to silver :

$$Ag_2HPO_3 + H_2O \rightarrow 2Ag + H_3PO_4.$$

2. **Barium chloride** gives a white precipitate of barium phosphite, $BaHPO_3$. (Cf. hypophosphites, 346.)

3. Mercuric chloride is reduced to mercurous chloride, and this,

further, to mercury, while the phosphorous acid is oxidised to H_3PO_4.

$$Hg^{\cdot\cdot} + HPO_3'' + H_2O \rightarrow Hg + HPO_4'' + 2H^{\cdot}.$$

346. Hypophosphorous acid. DRY REACTION. Use sodium hypophosphite, NaH_2PO_2. Hypophosphorous acid and hypophosphites when gently heated in a dry tube give off phosphine, leaving a phosphate :

$$2H_3PO_2 = H_3PO_4 + PH_3.$$

REACTIONS IN SOLUTION. H_2PO_2'.

1. **Silver nitrate** gives with neutral solutions a white precipitate of silver hypophosphite, AgH_2PO_2, which becomes black at ordinary temperature, rapidly on boiling :

$$2Ag^{\cdot} + 2H_2PO_2' + 4H_2O \rightarrow 2Ag + 2H_3PO_4 + 3H_2.$$

2. **Mercuric chloride** is reduced to mercurous chloride and mercury, the acid being oxidised to H_3PO_4.

3. **Barium chloride** gives no precipitate.

4. **Copper sulphate,** added to an acidified solution of a hypophosphite and warmed, is reduced to copper hydride which is thrown down as a chocolate brown precipitate :

$$2H_3PO_2 + 2CuSO_4 + 3H_2O = 2H_3PO_4 + H_2SO_4 + H_2SO_3 + Cu_2H_2.$$

Phosphites do not give this precipitate.

(Copper hydride is decomposed by hydrochloric acid, hydrogen being liberated.)

Arsenious acid and arsenic acid. (See 308.)

CONFIRMATION OF ARSENITES, ARSENATES AND PHOSPHATES TOGETHER

To the solution add magnesia mixture. Arsenates and phosphates are precipitated. Filter, acidify the filtrate and pass sulphuretted hydrogen. A yellow precipitate confirms arsenite.

Wash the precipitate of arsenate and phosphate, dissolve it in hydrochloric acid, reduce the arsenate with sulphur dioxide (see 308), boil off the excess of sulphur dioxide and divide the solution

into two parts. Through one pass sulphuretted hydrogen; a yellow precipitate confirms arsenate. Confirm phosphate in the other part by the ammonium molybdate test. A yellow precipitate should be formed at once or on warming with the hand.

Arsenates give with silver nitrate in neutral solutions a reddish brown precipitate.

347. Boric acid. DRY REACTIONS. Use borax (sodium diborate), $Na_2B\,O_7\,.\,10H_2O$.

1. Borax when heated froths up, loses the water and leaves a colourless transparent bead: this when moistened with cobalt nitrate and remelted forms a blue metaborate (353):

$$Na_2B_4O_7 + CoO = 2NaBO_2 + Co(BO_2)_2.$$

2. Place a little of the borate in a porcelain dish, add a few drops of conc. **sulphuric acid** and a little **methylated spirit**, stir and apply a flame to the mixture. A green flame is obtained.

3. A better test than the above is to mix, to a stiff paste, a small quantity of the borate with calcium fluoride and a drop of concentrated sulphuric acid, and hold it on platinum wire near the bottom of the Bunsen flame. Boron fluoride is liberated, which colours the flame green.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
$$B_2O_3 + 6HF = 3H_2O + 2BF_3.$$

4. Boric acid (liberated from a borate by addition of an acid) gives a brown stain on **turmeric** paper. The stain becomes greenish black on addition of an alkali.

REACTION IN SOLUTION. $\mathbf{BO_2'}$. Salts of orthoboric acid, H_3BO_3, are unknown in the pure state. Those in use are derived from metaboric acid, HBO_2, or pyroboric acid, $H_2B_4O_7$.

Silver nitrate gives a white precipitate of metaborate, soluble in ammonium hydroxide and in nitric acid. On boiling, the precipitate turns brown and finally black owing to hydrolysis.

$$Na_2B_4O_7 + 2AgNO_3 + 3H_2O \rightarrow 2AgBO_2 + 2H_3BO_3 + 2NaNO_3.$$
$$2AgBO_2 + 3H_2O \rightarrow Ag_2O + 2H_3BO_3.$$

348. Silicic acid. DRY REACTIONS. Use sodium silicate, Na_2SiO_3.

1. Heated on charcoal, moistened with cobalt nitrate and reheated, silica and silicates give a blue mass on fusion (cf. aluminium, **314, 1**).

2. Mixed with a **fluoride** and heated with concentrated **sulphuric acid**, silicon tetrafluoride is produced (see fluorides, **334, 2**). This test must not be carried out in a glass vessel.

3. Heated in a **microcosmic** bead, silica does not dissolve, and silicates decompose slowly, leaving free silica (**183**).

4. Heated with **sodium carbonate**, soluble silicates are produced.

REACTIONS IN SOLUTION. **SiO_3''.** Use soluble glass, Na_2SiO_3.

1. **Hydrochloric acid** liberates the silicic acid, which remains in solution in a colloidal state. On evaporation, the insoluble silica gel is produced.

2. **Ammonium carbonate** gives a precipitate of silicic acid on boiling, ammonia being evolved.

3. **Silver nitrate** produces orange-coloured silver silicate, Ag_2SiO_3, which is soluble in ammonium hydroxide and nitric acid.

349. Hydrogen peroxide. H_2O_2. REACTIONS.

1. Hydrogen peroxide decomposes on heating, especially in presence of alkalis, oxygen being evolved.

2. To a solution of hydrogen peroxide (or sodium peroxide dissolved in water, using proper precautions) add dilute **sulphuric acid**, a little **ether**, and one or two drops of potassium **dichromate** solution, and shake. A deep blue colour, due to perchromic acid, $HCrO_5$, is given to the layer of ether.

3. **Potassium iodide** added to an acidified solution of the peroxide yields iodine. Even in very dilute solution this is detected by means of starch paste.

4. **Potassium permanganate**, acidified with sulphuric acid, is at once decolorised by hydrogen peroxide, oxygen being evolved in equal amounts from both substances (**317, 438, 558**).

350. Metallic oxides and hydroxides. The oxides of heavy metals are practically insoluble in water, and are variously coloured. The oxides of zinc, tin and aluminium are white, zinc oxide becoming yellow on heating. Most of them dissolve readily in hydrochloric acid.

The oxides of the alkali metals and alkaline earth metals also are white, and unite with water, with evolution of heat, to form soluble hydroxides, the solutions having an alkaline reaction. Magnesium oxide is very sparingly soluble, and faintly alkaline in reaction.

Oxides of the alkali metals also unite with water, with evolution of heat, forming the caustic alkali hydroxides. These in the solid form are deliquescent, and absorb carbon dioxide from the atmosphere.

Soluble hydroxides may be detected by means of phenolphthalein, which colours the solution. In presence of alkali carbonates, which give hydroxyl ions by hydrolysis, the carbonate may be precipitated by addition of calcium chloride, and the solution then tested for hydroxides.

Hydroxides of heavy metals give up water on heating, and in general leave anhydrous oxides.

351. Metallic peroxides. Peroxides of the metals may be defined as oxides which contain more oxygen than those corresponding to the stable series of salts of the metals. Thus Mn_3O_4, Pb_3O_4, PbO_2 are peroxides, but not Fe_2O_3 or SnO_2.

Most peroxides evolve a portion of their oxygen when heated alone. They are not affected by cold dilute acids, but when heated with concentrated sulphuric acid they give off oxygen, and with concentrated hydrochloric acid they yield the equivalent amount of chlorine. Unstable salts are probably formed first and then decomposed :

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The true peroxides, such as BaO_2 and Na_2O_2, correspond to

hydrogen peroxide, which may be obtained from them by the action of dilute acids.

352. Per-acids and salts. Such substances as ammonium persulphate and sodium perborate are frequently used as oxidising and bleaching agents. Like the peroxides, most of them liberate oxygen on heating, leaving a salt of the normal acid from which the name is derived. Thus potassium percarbonate on heating evolves oxygen and carbon dioxide, leaving potassium carbonate :

$$2K_2C_2O_6 = 2K_2CO_3 + 2CO_2 + O_2.$$

Sodium perborate, $NaBO_3$, evolves oxygen readily at 100°, leaving borax and caustic soda. The cold aqueous solution contains hydrogen peroxide and is alkaline.

$$BO_3' + H_2O \rightarrow BO_2' + H_2O_2.$$

Potassium persulphate similarly decomposes in a warm solution, leaving sulphate :

$$2K_2S_2O_8 + 2H_2O = 2K_2SO_4 + 2H_2SO_4 + O_2.$$

Most of these salts also liberate iodine from potassium iodide, more or less rapidly :

$$C_2O_6'' + 2I' = 2CO_3'' + I_2,$$

and oxidise ferrous ions into ferric ions (312). By reference to these characteristics they may be easily identified.

A METHOD OF ANALYSIS

353. Preliminary examination. The substance should be carefully described before proceeding with the tests.

EXPERIMENT	OBSERVATION	INFERENCE
Heat a little of the substance in a dry tube	Fusion	Salts of the alkalis and some salts of Ba, Sr, and Ca. Also salts containing water of crystallisation

EXPERIMENT	OBSERVATION	INFERENCE
	A colourless liquid condenses in the cooler portions of the tube	Salts containing water of crystallisation
	The liquid is alkaline	NH_4 salts
	The liquid is acid	Acid salts, or substances liberating acidic oxides (nitrates, sulphates, etc.)
	A gas is evolved :	
	oxygen	Some oxides : peroxides, nitrates, chlorates, per-salts, etc.
	ammonia	NH_4 salts
	sulphur dioxide	Bisulphites ; sulphites or sulphates of heavy metals
	sulphuretted hydrogen	Some sulphides in presence of water
	nitrogen dioxide (brown)	Nitrates of heavy metals
	chlorine	Chlorides with oxidising agents, some chlorates and hypochlorites
	bromine (red-brown)	Bromides in presence of oxidising agents
	iodine (violet)	Iodides or free iodine
	carbon dioxide	Carbonates of heavy metals, bicarbonates, oxalates, etc.
	carbon monoxide	Formates, oxalates
	cyanogen	Some cyanides
	A sublimate is formed	
	white	NH_4, Hg, As compounds
	white, with irritating fumes	Oxalic acid, etc.
	yellow	As_2S_3, HgI_2 (red when rubbed)
	yellow (which melts on heating)	Free S, or from thiosulphates or sulphides
	metallic mirror (small beads)	Hg
	dark grey mirror	As, Sb
	The residue is	
	white, fusible	Salts of the alkalis and some salts of Ba, Sr, Ca
	white, infusible	Ba, Sr, Ca, Zn, Al, Mg
	white, „ yellow hot	ZnO
	yellow, fusible, reddish brown when hot	PbO, Bi_2O_3
	red-brown, black hot	Fe_2O_3
	brown, darker hot	CdO, Mn_3O_4
	yellow, darker hot	SnO_2
	black	CuO, Co_3O_4, NiO
	charred : perhaps tar	Organic matter

EXPERIMENT	OBSERVATION	INFERENCE
Heat a little of the substance on platinum wire, first dipping the wire in HCl	Flame, bright yellow	Na
	lambent blue	Pb, Cu, Sb, As, Bi, Cd, Zn
	deep blue	Se
	green, blue-green	Ba, Tl, B_2O_3, Cu
	dull red	Ca
	crimson	Sr, Li
	lilac	K, Rb, Cs
Heat a little of the substance on charcoal in the reducing flame	Decrepitation	NaCl, $Pb(NO_3)_2$, and many anhydrous salts
	Deflagration	Nitrates, nitrites, chlorates
	Metallic bead formed :	
	greyish white, malleable, marks paper	Pb
	white (red tinge), brittle	Bi, Sb
	white, hard	Ag, Sn
	An incrustation is formed :	
	white	Sb, NH_4 salts
	white (volatile, garlic odour)	As
	white, yellow hot	Zn, Sn, Mo
	yellow, orange hot	Bi
	yellow-brown	Cd
	The residue is	
	fusible	Salts of alkalis
	white, infusible	Ba, Sr, Ca, Zn, Al, Mg
	coloured	Cu, Fe, Cr, Co, Ni, etc.
If the residue is white, moisten with $Co(NO_3)_2$ and reheat	blue mass	Al (possibly phosphates, borates) silicates
	green mass	Zn, Ti, Sn
	pink mass (difficult)	Mg
If the residue is not white, heat a little of the original substance in a borax or microcosmic bead	The bead is in the	
	Oxidising flame	*Reducing flame*
	amethyst	colourless — Mn
	reddish brown	grey — Ni
	greenish blue	red — Cu
	yellow, red when hot	yellow (hot) — Fe
		bottle-green (cold)
	green	green — Cr
	blue	blue — Co

EXPERIMENT	OBSERVATION	INFERENCE
Boil a little of the substance with NaOH soln.	NH_3 is evolved	NH_4 salts Possibly cyanides, amides, urea
Boil till no more NH_3 is evolved; and /or if none, add Al foil and boil again	NH_3 is evolved	Nitrates, nitrites
Warm a little of the substance with dilute HCl	Effervescence (gas evolved): CO_2 (tested with lime water) SO_2 SO_2 and S pptd. H_2S brown fumes chlorine hydrogen HCN	Carbonate Sulphite Thiosulphate Sulphide Nitrite Hypochlorite; oxidising agents, chlorate, peroxide Some metals Cyanide
Warm a little of the substance with conc. H_2SO_4	Acid fumes (test for HCl by adding MnO_2): Cl_2 CO_2 CO O_2 chromyl chloride (red) red fumes red fumes, with chlorine (bleaches) violet fumes crackling in tube, and greenish yellow gas SO_2 H_2S S greasy appearance in the tube charring with evolution of CO_2 and SO_2 odour of acetic acid	Chloride, bromide (give Br also), nitrate, fluoride Chloride in presence of an oxidising agent Carbonate, oxalate, etc. Oxalate, formate, ferrocyanide Peroxide or per-salt Chloride in presence of chromate Nitrite or bromide Nitrate in presence of chloride Iodine or iodide Chlorate Sulphite, thiosulphate or reducing agent Sulphide or reducing agent Reduction of H_2SO_4 Fluoride Tartrate, Citrate Acetate

354. Further examination for anions. In the preliminary tests, many ions have been shown definitely to be present or to be absent. Arsenic may have been indicated by the charcoal test, and if so will be confirmed in the group separation. Phosphates and silicates have also been tested for during the separation of metals into groups and possibly suspected previously. The absence of other anions may be deduced from the nature of the cations found, together with the solubility of the substance. Thus a substance soluble in water or acids cannot contain barium and a sulphate, and if silver be present, chlorides, bromides and iodides must be absent.

If a sulphite has been found, test for a carbonate by **337**, 4.

If the water extract is alkaline and a carbonate is present, test for hydroxides as in **350**.

To test for a sulphite in presence of a thiosulphate, see **341**.

To a solution of the substance in water acidified with HNO_3 or to a solution of the substance in HNO_3, add $AgNO_3$	White precipitate (readily sol. in NH_4OH). V. pale yellow ppt. (sol. in NH_4OH). Pale yellow ppt. (insol. in NH_4OH). Orange yellow ppt. (sol. in NH_4OH)	Cl', CN', SCN' $Fe(CN)_6''''$ Br' I' $Fe(CN)_6'''$

To detect bromides in presence of iodides, and chlorides in presence of bromides and iodides, see **333**, 5.

To detect chlorides in presence of cyanides and complex cyanides, see **373**.

To a solution of the substance in water acidified with HCl or to a solution of the substance in dilute HCl, add $BaCl_2$	White ppt.	SO_4''

Whether or not a greasy appearance in the tube has been noticed, fluoride should be confirmed by **334**, 2, with the original substance and if found confirm sulphate by dry reaction **339**. If sulphides, sulphites or thiosulphates have been found, remove them (see **338, 339, 341**) before trying this test.

Confirm nitrate by the brown ring test (**343**, 4), but if nitrites, bromides or iodides are present, refer to **343**, 6.

Test for borate by **347**, 3.

Neutral solution. In some cases the presence of certain cations interferes with the silver nitrate test (*e.g.* ferrous salts give a black precipitate of silver). In these cases, and also where further confirmation of certain anions or perhaps cations is desired (arsenic, thiosulphuric, etc.), a neutral solution may be made as follows: Boil a little of the substance for several minutes with a conc. solution of Na_2CO_3, filter, and *neutralise* the filtrate by adding HNO_3 in slight excess, boiling to expel CO_2, then adding NH_4OH in very slight excess, and boiling until quite neutral. The residue contains all the cations, and the anions are present in the filtrate in the form of sodium salts.

Portions of this neutral solution should be tested with $AgNO_3$ and $BaCl_2$. Although some of the anions indicated, such as Cl', Br', I', SO_4'', CO_3'', etc., have already been decided, and do not require the neutral solution, they are included for the sake of clarity.

Experiment	Observation	Inference
$AgNO_3$	A ppt. is obtained, insoluble in HNO_3 and	
	white (very soluble in NH_4OH)	Cl'
	pale yellow (soluble in NH_4OH)	Br'
	yellow (insoluble in NH_4OH)	I'
	The ppt. is soluble in HNO_3 and is	
	white	NO_2', SO_3'', CO_3'', BO_3'''
	black	S''
	yellow	PO_4''', AsO_3'''
	brown	S_2O_3''
	chocolate	AsO_4'''
	red	CrO_4''
$BaCl_2$	The ppt. is insoluble in HCl, and is	
	white	SO_4''
	The ppt. is soluble in HCl, and is	
	white	PO_4''', AsO_3''', AsO_4'''
		BO_3''', S_2O_3'', CO_3''
		SO_3''
	yellow	CrO_4''

FINAL EXAMINATION FOR CATIONS

355. Preparation of a solution. (If the substance is a liquid it should be examined by (*a*) testing with litmus, (*b*) evaporating a little to dryness to see whether solids are present, (*c*) applying the dry tests (353) to any residue.)

Take a *small* quantity of the substance, add water and boil.

If the substance is soluble in water, note its action on litmus. Test a little of the solution with sodium carbonate. If there is no precipitate, only alkali cations can be present ; but it is necessary to test for arsenite, arsenate, phosphate, chromate (yellow). Then proceed with the separation into groups.

If it does not dissolve, test the liquid with litmus paper ; if alkaline or acid, a portion has dissolved. If neutral to litmus, filter a few drops and evaporate to see whether a part has dissolved. Now add a little dilute HCl to the substance and boil for a few minutes. If a residue is left, boil further, add more water and boil again.

If the substance is insoluble in dilute HCl, boil a fresh quantity with concentrated HCl for several minutes, add water and boil.

If not entirely soluble, boil another portion with aqua regia, evaporate nearly to dryness, add a little concentrated HCl, and evaporate to a small bulk to remove HNO_3. Dilute with water.

If yet some or all remains undissolved, warm a little with concentrated HNO_3, dilute and boil ; if soluble add HCl. A white precipitate, if formed, should be tested for the silver group, and the HCl (or aqua regia) solution proceeded with for the other groups.

In many cases it will be advantageous to treat the water or HCl extract separately from that obtained by aqua regia, as the number of substances insoluble in HCl but soluble in aqua regia is very limited, and those may often be easily identified.

356. Separation of the cations into groups. To the cold solution add a few drops of HCl (if the substance has been dissolved in HCl this is unnecessary). If a precipitate is produced add more acid till there is no further precipitate, cool well and filter.

Precipitate: May consist of
$PbCl_2$ (white)
AgCl (white)
HgCl (white)

Examine by table for the silver group

Solution: If HNO_3 is present evaporate nearly to dryness to expel it. If arsenate is suspected confirm by 308, 5; if present reduce with H_2SO_3, boil off SO_2 and saturate with H_2S. Test a little of the filtrate by diluting and again passing H_2S.

Precipitate: May consist of
HgS (yellow, finally black)
PbS (black, may be red)
CuS (black)
Bi_2S_3 (dark brown)
CdS (yellow)
As_2S_3 (yellow)
Sb_2S_3 (orange red)
SnS (dark brown)
SnS_2 (dull yellow)
S (very pale yellow)
Solution changes colour from yellow to green, chromates;
from yellow to pale green or colourless, ferric salts
In both cases sulphur is pptd.
Examine by table for copper group

Solution: Boil off H_2S, concentrating the liquid if bulky. Add 2 or 3 drops of conc. HNO_3 and boil. Test a little of the solution for phosphates with ammonium molybdate (344). To the remainder of the solution add NH_4Cl, boil, add slight excess of NH_4OH, boil, and filter immediately. (The ppt. may be due to organic substances, silicates, etc. If these are present they should be eliminated after passage of H_2S by evaporating to dryness and igniting.)

Precipitate: If phosphates are absent, may consist of
$Fe(OH)_3$ (reddish brown)
$Cr(OH)_3$ (grey-green)
$Al(OH)_3$ (white)
Examine by table for iron group
If phosphates are present, all the metals of the iron, zinc and barium groups and magnesium may be pptd. as phosphates together with the above hydroxides
Examine by phosphate table

Solution: At once pass H_2S

Precipitate: May consist of
CoS (black)
NiS (black)
MnS (flesh coloured)
ZnS (white)
Examine by table for zinc group

Solution: Add NH_4OH till the liquid smells of NH_3, then $(NH_4)_2CO_3$ till no further ppt.; warm (do not boil) and allow to stand for ten minutes

Precipitate: May consist of
$BaCO_3$ (white)
$SrCO_3$ (white)
$CaCO_3$ (white)
Examine by table for barium group

Solution: May contain Mg, K, Na, Li
Examine by table for sodium group

357. Separation of the silver group cations. Wash the precipitate with cold water ; then pour on 10 c.c. boiling water, collecting the hot filtrate. Heat this again, and again pour over the precipitate.

Solution : May contain $PbCl_2$	*Residue* : Pour over it a small quantity of NH_4OH
Cool with shaking under the tap ; white needle-shaped crystals separate. **Pb is present** If no ppt. on cooling, add K_2CrO_4 ; yellow ppt. of $PbCrO_4$	*Solution* : Acidify with HNO_3 ; white ppt. **Ag is present**
	Residue : Black Hg + NH_2HgCl or NH_2Hg_2Cl **Hg is present** Dissolve in small quantity of aqua regia, dilute largely and place in the solution a clean strip of copper Grey deposit of mercury

358. Separation of the copper group cations. Wash well with hot water, boil about 10 c.c. of yellow ammonium sulphide (if tin and mercury are absent, sodium hydroxide may be used), pour it over the precipitate and collect the filtrate ; boil this and again pour over the precipitate. Repeat if necessary.

Residue : Wash well, transfer to a test-tube, add a little conc. HNO_3, heat till red fumes cease, dilute. Test a few drops for lead with dilute H_2SO_4 and alcohol. If lead is present mix the whole of the liquid with H_2SO_4 (a few drops) and alcohol (an equal bulk), and allow to stand for 10 minutes in the cold

Solution : Acidify with dilute HCl ; a flocculent ppt. shows the presence of As, Sb, or Sn. Boil the moist ppt. with $(NH_4)_2CO_3$ solution and filter

Residue : If lead is present, warm with ammonium acetate

Solution : If alcohol has been added, boil this off, add excess of NH_4OH and warm ;

Solution : Acidify with HCl. Yellow ppt. of As_2S_3 Dissolve in a small quantity of aqua regia, evaporate to expel most of the acid, add excess of ammonia, filter if necessary and add magnesia mixture. White cryst. ppt. of $Mg(NH_4)AsO_4 6H_2O$ **As** is present

Residue : Boil with conc. HCl ; dilute and filter if necessary. Divide into two parts

i. Make just alkaline with NH_4OH, add a few grams oxalic acid, boil and pass H_2S. Ppt. orange coloured

Sb is present

ii. Dilute with water, add 12″ iron wire and warm for some minutes to reduce $SnCl_4$ to $SnCl_2$. Filter into $HgCl_2$ solution White (HgCl) or grey (Hg) ppt.

Sn is present

Residue : Dissolve in a little aqua regia, dilute and place in the solution a bright strip of copper. Grey deposit, which becomes bright on rubbing

Hg is present

Solution : Add K_2CrO_4 Yellow ppt.

Pb is present

Precipitate : Pour over it a few drops of sodium stannite solution ($SnCl_2$ + excess NaOH) : the ppt. is blackened,

Bi is present

Solution : If colourless, Cu is absent ; pass H_2S, yellow ppt.—**Cd** is present

If blue, **Cu** is present ; divide the solution into two parts

To one part add acetic acid in excess and $K_4Fe(CN)_6$; brown ppt., **Cu** is present

To the other part add KCN till colourless and pass H_2S ; yellow ppt.

Cd is present

359. Separation of the iron group cations (phosphates being absent). Wash well, pour a little warm dilute HCl over the precipitate several times to dissolve the hydroxides; to this solution add sodium peroxide carefully, in small quantities, until in excess, boil and filter.

Precipitate: Reddish brown, **Fe** is present Dissolve in HCl and add $K_4Fe(CN)_6$; dark blue ppt. NOTE.—$Mn^{..}$ is so easily oxidised in presence of alkali that it is usually pptd. in the iron group as Mn_2O_3. In this case Na_2O_2 produces black MnO_2, and even a trace of this will darken the brown $Fe(OH)_3$	Solution may contain sodium chromate and aluminate. Divide into two parts (1) Yellow solution **Cr** is present Add acetic acid in excess, and lead acetate; Yellow ppt. (2) Add 2 or 3 drops of litmus solution, acidify with HCl and add NH_4OH till alkaline White ppt. of $Al(OH)_3$, forming a "lake" with the colouring matter; **Al** is present

360. Separation of the cations pptd. in the iron group (phosphates being present). Wash well, dissolve in the smallest possible quantity of warm dilute HCl, dilute, add NH_4OH, drop by drop, until the last drop produces a ppt. which does not redissolve when shaken. Add dilute acetic acid until just acid, and 1 or 2 c.c. of a conc. solution of ammonium acetate.

1. If the liquid is red, there is more than sufficient iron present to ppt. all the phosphate ion. Add ammonium phosphate to just ppt. all the iron, and then a drop or two of $FeCl_3$ till the solution is red. Boil for 10 minutes, or until the solution is colourless, and filter.

2. If the liquid is not red, add $FeCl_3$, drop by drop, until no further buff ppt. of $FePO_4$ is produced and the solution turns red. Boil as above and filter.

Precipitate: Consists of ferric phosphate and basic ferric acetate; and, if a ppt. was produced on the addition of ammonium acetate, $Al^{...}$ and $Cr^{...}$ may be present Examine for $Al^{...}$ and $Cr^{...}$ by table for the iron group (359) Test the original substance for $Fe^{..}$ and $Fe^{...}$	*Solution*: Examine for the Zn and Ba groups and for Mg as in 356

361. Separation of the zinc group cations. If the ppt. is not black, it may be dissolved in warm dilute HCl and tested for Mn and Zn only.

If black, wash the precipitate into a small porcelain dish with very dilute HCl (1 of acid to 5 of water), stir till no more H_2S is evolved.

Residue : Test in borax bead. If the bead is brown, Co is absent, Ni is present. Confirm by glyoxime test

If the bead is blue, cobalt is present. Since this blue colour is so intense as to mask about 30 times as much Ni, the latter must be tested for as follows. Wash the residue into a small porcelain dish, add a little conc. HCl and a crystal of $KClO_3$, and heat till the ppt. is dissolved. Evaporate the solution just to dryness and dissolve in a little water. Nearly neutralise with sodium carbonate (solid may be used to avoid increase of bulk), and divide the solution into two parts :

(1) Add 5 or 6 c.c. of dimethylglyoxime solution, make just alkaline with ammonia, and warm. A fine carmine ppt. of the Ni salt of dimethylgloxime ;

Ni is present

(2) Place in a porcelain dish, add a conc. solution of $NaNO_2$ and a little acetic acid. Warm gently till brown fumes cease, add KNO_3 solution and stir or allow to stand. Bright yellow ppt.

Co is confirmed

Solution : Boil till free from H_2S, add NaOH in excess, boil and filter

Residue : is $Mn(OH)_2$ Confirm by bead of sodium carbonate with a crystal of KNO_3 : green bead,

Mn is present

Solution : Pass H_2S ; white ppt.,

Zn is present

362. Separation of the barium group cations. Pour warm dilute acetic acid over the ppt. on the filter paper several times to dissolve the carbonates; add K_2CrO_4 until the liquid assumes the orange colour of $K_2Cr_2O_7$.

Precipitate: Yellow $BaCrO_4$ **Ba** is present Wash and test on platinum wire; green flame Dissolve in dilute HCl and add H_2SO_4 White ppt. of $BaSO_4$, insoluble even on boiling	*Solution*: Add 8N. $(NH_4)_2SO_4$; warm and allow the solution to stand ten minutes	
	Precipitate: White $SrSO_4$ **Sr** is present Wash and test on platinum wire; crimson flame Ca may be pptd. here if the solution is strong, but may be removed by dissolving in a warm conc. solution of ammonium sulphate	*Solution*: Add ammonium oxalate; white cryst. ppt. $CaC_2O_4 . H_2O$ **Ca** is present The flame test is important in this group

363. Separation of the sodium group cations. Divide the solution into two parts.

Smaller part : Add Na_2HPO_4 and allow to stand ; white crystalline ppt.

Mg is present

Filter, add NaOH to filtrate and boil ; white ppt. of Li_3PO_4

Li is present

Confirm by the flame test with the ppt., moistening it in HCl

NH_4 salts must always be tested for in the original substance or solution by boiling with NaOH

NH_3 is evolved

Larger part : Evaporate to dryness in a small porcelain or silica dish, and heat strongly to drive off the ammonium compounds

If no residue, K, Na, Li and Mg are absent

If a residue, test on platinum wire ; yellow flame, **Na** is present ;
lilac flame, **K** is present ;
crimson flame, **Li** is present

The flame of K may be identified in presence of the Na flame by using a blue glass or prism

If Na is present, a test for K should always be made. To do this, dissolve the residue in the smallest possible quantity of water, place on a watch-glass, add $PtCl_4$ and rub gently with a glass rod ; heavy yellow ppt. of K_2PtCl_6

Or instead of $PtCl_4$, add a little sodium cobaltinitrite solution in a watch-glass and stir ; yellow ppt. of $K_3Co(NO_2)_6$

K is present

Distinctive tests for the ions of different valencies derived from mercury, copper, arsenic, antimony and tin are given in pars. 303–310.

If iron has been found, the original substance should be examined to determine its valency, $Fe^{\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$. See 312.

If chromium has been found, see 313 for distinctions between $Cr^{\cdot\cdot\cdot}$, CrO_4'' and Cr_2O_7''.

Metallic powders such as zinc dust are usually indicated by their behaviour with acids in the preliminary tests. The metals of the iron and zinc groups, and tin, liberate hydrogen from HCl. Others require HNO_3 (Pb, Ag, etc.) for their solution, and a few dissolve only in aqua regia. Their identification should offer no difficulty.

364. Treatment of the insoluble portion. The insoluble substances include the following: SiO_2 and silicates, $BaSO_4$, $SrSO_4$, AgCl, AgBr, AgI, SnO_2, Sb_2O_4, As_2S_3 and CaF_2; also Fe_2O_3, Cr_2O_3, Al_2O_3 after intense ignition. Wash the insoluble residue well with hot water.

If the original substance has been treated with aqua regia, any silver bromide or iodide will now be changed to chloride; therefore if the residue be washed with ammonia this will be removed and may be reprecipitated by nitric acid.

If silver is found, take a little of the original substance, add H_2SO_4 and zinc, and leave in contact with the substance for 20 minutes. The silver will have been replaced by zinc, and the soluble zinc salts may now be tested for chloride, bromide and iodide.

Having removed the silver, fuse the residue on platinum foil with fusion mixture, and boil the product with water. Filter, and wash well. Proceed as in the table, p. 319.

Report on the analysis. The results obtained in the analysis should now be summarised in a short statement setting forth the salient properties of the substance. This report should not only show the cations and anions which are present, but should indicate, from a consideration of properties such as colour, crystalline form, deliquescence, solubility in various solvents, reaction to litmus, etc., the nature of the compounds which are actually present in the original substance.

Residue : May contain Fe_2O_3 (brown), $BaCO_3$, $SrCO_3$, and any unaltered SnO_2, CaF_2, etc. Boil with HCl

Solution : May contain silicate, aluminate, chromate (yellow), stannate, antimonate, arsenate, sulphate, and fluoride of sodium in addition to the Na_2CO_3 and K_2CO_3 of the fusion mixture. Divide into a large and a small portion

Residue :	*Solution* :
Brown, Fe_2O_3 Confirm by borax bead	Examine for Ba and Sr

SMALL PART	LARGE PART
Test for H_2SO_4 Test for silica and silicates by heating a small portion of the insoluble residue in microcosmic bead or by CaF_2 and H_2SO_4. (See tests for silicates, 348)	Examine for cations by separation into groups, etc., removing the silica by evaporation to dryness after the removal of the copper group

QUALITATIVE ANALYSIS OF ORGANIC SUBSTANCES

365. If these are present in a mixture with inorganic matter, the analysis becomes more complicated on both parts. In the examination for cations, organic matter must in general be destroyed (356), as it interferes with the precipitation of certain cations. On the other hand, organic substances are most easily detected in the absence of inorganic salts, and the examination for organic anions should be made in a solution containing no cations other than those of the alkali group. The preparation of such a solution is described hereafter. In the following scheme, the substance under examination is assumed to be entirely or mainly organic. The tests are applied not necessarily in the order given ; a little experience will suggest the best method for each case.

DETECTION OF THE ELEMENTS

366. The elementary composition of a substance affords valuable suggestions as to its nature, and the following tests should always be made, unless other evidence renders them unnecessary.

Carbon and hydrogen. These elements may be assumed to be present, but may be detected by heating a little of the substance with a few grams of dry copper oxide, or lead chromate (if sulphur or halogens are suspected), and passing the evolved gas into lime water or baryta water. A white precipitate of carbonate is formed. Moisture condenses in the top of the ignition tube.

Carbon and hydrogen alone are present in the hydrocarbons. In addition to these, oxygen is present in the carbohydrates, alcohols, phenols, aldehydes and ketones, ethers, esters, and carboxy-acids.

Nitrogen. This element is present in the proteins, amino-acids (glycine), amides and amines, alkaloids and purine derivatives (uric acid), and many dyestuffs.

1. Some of these evolve ammonia or alkaline and pungent smelling vapours on being heated in a test-tube with soda-lime.

2. Cyanide (Lassaigne's) test. Heat a little of the substance in a dry test-tube with a small pellet of sodium until all action has ceased. To avoid loss of nitrogen from volatile or easily decomposable compounds, the portion should be dropped directly on to the molten sodium in a test-tube held vertically in a clamp. When cool, add 2 or 3 c.c. alcohol to remove the excess of sodium, and wait till no more hydrogen is evolved. Add water, boil and filter; divide the filtrate into three parts. Retain two parts to test for sulphur and halogens (below). To the other part add a little $FeSO_4$ solution, and then a few drops of $FeCl_3$ solution, and acidify with dilute HCl. A blue or blue-green colour, or a precipitate of Prussian blue, indicates the presence of nitrogen.

Sulphur is present in the proteins, mercaptans and thioethers, sulphonic acids, etc.

1. To one-third of the solution from the sodium fusion (above) add a few drops of sodium nitroprusside solution. A violet coloration indicates sulphur. Lead in alkaline solution is also a delicate test (**338, 4**).

2. Mix about half a gram of the original substance with a gram of KNO_3 or Na_2O_2, and 3 grams fusion mixture, and fuse in a silica crucible until all carbon is burnt away. On cooling,

dissolve in water and divide into two parts. To one part add HCl in slight excess, and $BaCl_2$ solution. A white precipitate of $BaSO_4$ indicates sulphur.

Phosphorus. To the other part of the solution from the peroxide fusion, add HNO_3 and excess of ammonium molybdate, and warm. A yellow precipitate of ammonium phosphomolybdate indicates phosphorus.

The halogens. 1. The remaining one-third of the solution from the sodium fusion is acidified with HNO_3 when the addition of $AgNO_3$ solution will indicate the presence of halogens. These may be distinguished by the method given in **333.**

2. Most halogen derivatives, when heated on the end of a copper wire previously oxidised in the Bunsen flame, give a bluish-green colour.

Metals. Heat a little of the substance on platinum foil or a silica tray until all carbon is burnt away. Any residue will consist of alkali carbonates or the oxides of heavy metals. Moisten with water and test with litmus paper. Add a drop of HCl and note whether CO_2 is evolved. The metals present are detected in the ordinary way (353), and heavy metals must be removed before testing for the organic acids.

Some of the above tests may be difficult or impossible to apply to volatile substances in the manner described. In such case a modification of the test may be devised, or other evidence relied upon for the identification.

367. The action of heat and some general reactions. 1. In the case of liquids, evaporate a little carefully on a watch-glass or porcelain dish. Note whether inflammable vapours come away (most volatile liquids), acid fumes (formic, acetic), and observe the nature of the flame ; also whether a residue is left, and its nature. A syrupy residue with sweetish taste will indicate glycerol or sugars. Formaldehyde (formalin) leaves a white amorphous residue. Solutions of solid organic substances, in water or other liquids, will leave a solid residue, which may then be examined further.

2. Heat the substance alone in a dry tube.

Substance melts and chars: emits smell of burnt sugar	Sugars, tartaric or citric acids. Starch chars without melting
Irritating vapours are evolved	Citric, oxalic, succinic acids: glycerol
Substance melts and forms a white sublimate	Free oxalic, succinic, benzoic or salicylic acids: phenol
Substance melts and evolves ammonia	Urea and ammonium salts: uric acid does not melt, but chars, emitting NH_3 and HCN

Phenol and aniline give characteristic odours.

3. Heat the substance with 3 or 4 times its weight of powdered soda-lime:

An inflammable gas is evolved	Formic, acetic, oxalic or benzoic acids: the last gives benzene
Ammonia liberated, or alkaline vapours	Urea, amides, uric acid, aniline, alkaloids, glycine
Odour of aniline	Aniline (or salts): acetanilide
Odour of phenol	Phenol or salicylic acid

4. Mix the substance with cold concentrated H_2SO_4.

CO evolved	Formate
Smell of acetic acid	Acetate
Now warm gently:	
CO and CO_2 evolved, charring and odour of burnt sugar, with CO_2 and SO_2; liquid darkens slowly; odour of burnt fat (acrolein)	Oxalate, citrate, urate, sugars, starch, tartaric acid — citrates and succinates char slowly; benzoate, salicylate; glycerol

Physical properties, such as melting point, boiling point and specific gravity, are of great importance (Section I), and should be used finally to identify a pure substance. Two liquids may usually be separated by fractional distillation, the boiling points being noted, or a liquid may be separated from a solid in this way.

The melting point of a solid should be compared with that of the substance it is supposed to be, and at the same time the melting point of a mixture of the two should be taken. If the two are identical, the melting point will not be affected; if not, the melting point will in general be depressed.

The **odour** is very characteristic for many substances, such as alcohols, ethers, ethereal salts, and should be carefully observed, as well as the colour and general appearance.

The **solubility** should be examined carefully. Shake up a little of the substance vigorously with cold water, and if necessary separate the aqueous layer from the remaining liquid, or filter from the remaining solid. Test the aqueous liquid with litmus: an acid reaction will indicate free acids or acid salts, such as bi-tartrates, aniline salts or some alkaloid salts; an alkaline reaction may indicate alkali salts of some organic acids, or basic substances. The aqueous solution will also contain the simpler alcohols and aldehydes, glycerol, acetone, phenols, sugars. Insoluble or sparingly soluble in water are the hydrocarbons, ethers, the higher aliphatic alcohols and aldehydes, ketones and esters; aromatic derivatives of these classes, starch, alkaloids and aromatic bases.

If an alcohol, aldehyde, or acetone is suspected from the solubility and the smell, it should be confirmed by the special tests already given. Choral hydrate, an odourless solid, soluble in water, behaves as an aldehyde, and will have indicated chlorine in the detection of elements. Ethereal salts are generally insoluble and must be saponified, the alcohol distilled off and oxidised to aldehyde or acid for identification, and the alkaline residue in the flask examined for the original acid.

Glycerol if present may be recovered from the aqueous solution by careful evaporation, and confirmed by the borax or acrolein tests.

If the substance does not dissolve in cold water, try the effect of hot water. Starch is converted into a paste, which on cooling gives a blue colour with iodine solution. Confirm by hydrolysis to glucose.

Further, warm the substance insoluble in water with solution of NaOH or KOH. Aromatic acids and phenols dissolve: NH_3 is evolved from urea, acid amides, and ammonium salts. Urea is confirmed by its special reactions, amides boiled until decomposition is complete, and the acids identified as described below.

If nitrogen is present, and no ammonia is evolved on boiling

with alkalis, aniline, acetanilide, uric acid, glycine or alkaloids may be present, and may be detected by their specific tests. Aniline is liberated from its salts by alkalis, and may be removed from the solution, in cases where it interferes with the detection of other substances, by distilling with steam or extracting the cold solution with ether. Acetanilide is a substituted amide, and under the treatment with alkali decomposes into aniline and alkali acetate. The aniline, in this case also, may be extracted, and the residual alkaline liquor tested for acetate. If no aniline is found, the substance may be glycine (see this).

A scheme for the detection of the commoner alkaloids is given later.

If the substance is insoluble in alkali, the smell may indicate benzyl alcohol or benzaldehyde, which may be identified by their special reactions, and by oxidation to benzoic acid. Ether also gives none of the above reactions, and may be identified by smell and boiling point; hydrocarbons, if present, will probably be aromatic, and may be converted into nitrocompounds (nitrobenzene).

Halogen derivatives as a rule are insoluble in alkali ($CHCl_3$, CHI_3, C_2H_5I), and are recognised by physical and other tests, which are given for each. They are, however, decomposed on boiling with alkali. Choral hydrate thus readily decomposes into chloroform and a formate. If none of these is present, and yet the substance contains chlorine, chloroacetic acid may be looked for (see 215).

DETECTION OF ORGANIC ACIDS

368. If the substance does not dissolve in water, free benzoic or salicylic acids may be present. These will dissolve on addition of NaOH or Na_2CO_3. If insoluble in alkali, salts of heavy metals may be expected. In this case dissolve in the minimum of dilute HCl, or HNO_3, add excess of Na_2CO_3 solution and boil. This precipitates the heavy metals, and, at the same time, liberates aniline and the alkaloids from their salts. Phenol does not unite with alkali carbonate. These, if present, should be extracted with ether before proceeding with the analysis.

In some cases, however, the metals are not precipitated by Na_2CO_3, as Hg in presence of cyanides, Sb in tartar emetic, Fe, etc., in presence of tartaric or citric acids or sugars. In such cases the metals must be removed by treatment with H_2S first in acid and then in ammoniacal solution, and this followed by boiling with sodium carbonate. The filtrate is then rendered neutral by adding HNO_3 in slight excess, boiling to expel CO_2 and H_2S, making slightly alkaline with NH_4OH, and finally boiling till quite neutral.

369. Calcium chloride group. To a portion of the neutral solution add acetic acid and cool well. A precipitate of potassium hydrogen tartrate may be produced, if K_2CO_3 was employed instead of Na_2CO_3. Filter. To the filtrate add $CaCl_2$ solution in excess.

An immediate white precipitate of calcium oxalate indicates **Oxalic acid** Confirm by placing the precipitate in dilute sulphuric acid, warming to 70°, and adding a solution of $KMnO_4$ drop by drop. This is decolorised by oxalic acid	To the filtrate add NH_4OH in slight excess, cool, shake well and allow to stand for 15 minutes. A white crystalline precipitate of calcium tartrate separates. Confirm by warming a portion of precipitate with H_2SO_4 and a small quantity of pyrogallol. Violet coloration indicates **Tartaric acid** Confirm also by the reduction of ammoniacal silver solution	To the filtrate add more calcium chloride if the other acids have been found, and boil to a small bulk ; a white precipitate gradually forming indicates **Citric acid** Confirm by warming the precipitate with conc. H_2SO_4. Citric acid is slowly charred

370. Ferric chloride group. To another portion of the neutral solution add neutral ferric chloride solution, observing first the effect of one drop of the reagent. A distinct yellow colour is given by aliphatic hydroxy-acids, as lactic, malic, citric, tartaric. With excess of ferric chloride :

A red-brown colour —Formate, acetate, chloroacetate or glycine : on boiling, the brown basic ferric salt is pptd.

A violet colour —Salicylate or phenol.
A buff-coloured ppt., soluble in NH_4OH. —Benzoate.
A bulky brown ppt. —Succinate.

If a precipitate is obtained with $FeCl_3$ in the cold, filter and boil the precipitate with NH_4OH ; filter :

Residue is a more basic succinate and/or ferric hydroxide	Solution may contain some ammonium succinate or benzoate. Add an equal bulk of alcohol and a little $BaCl_2$. A white ppt. indicates succinate (benzoate gives no ppt.)

These acids may be confirmed by special tests, such as

Formic acid —Reducing properties.
Acetic —Ethyl acetate reaction.
Chloroacetic —Detection of chlorine in the ppt.
Glycine —Detection of NH_2 group in the ppt.
Salicylic acid —Ethyl or methyl salicylate : Br water.
Phenol —Br water ; Liebermann's test.
Benzoic acid —Ethyl benzoate reaction.
Succinic —Resorcinol test.

These confirmatory tests are described among the reactions for the several acids, and reference should be made to them when required.

371. Carbohydrates. If more than one of these be present in the same solution, they may be detected as follows :

To a neutral solution add a few drops of iodine solution :

<table>
<tr><td rowspan="3">Blue colour—starch
Confirm by hydrolysis followed by reduction of Fehling's solution</td><td colspan="2">If starch is present, extract soluble sugars from the original substance with cold water and filter ; to this filtrate, or to the prepared solution if starch is absent, add Fehling's solution and warm</td></tr>
<tr><td>Red ppt. of Cu_2O
Glucose
Confirm by the osazone and fermentation tests</td><td>If glucose has been found, boil with Fehling's solution until no more ppt. is thrown down. Filter. Apply the inversion test for cane sugar, followed by Fehling's test</td></tr>
</table>

372. The alkaloids. These if present should first be isolated by careful addition of NaOH or NH_4OH to the aqueous or HCl solution of the substance. See also pars. **295-300.**

The precipitate is filtered and washed with cold water. Test this precipitate as follows :

1. Place a little in a porcelain basin, and stir with a drop of strong HNO_3. An intense red coloration indicates :

Morphine	*Brucine*
Unchanged by $Na_2S_2O_3$ Confirm by reactions with (*a*) $FeCl_3$—blue colour (*b*) HIO_3—brown colour	Changed to violet by $Na_2S_2O_3$ Confirm by (*a*) $FeCl_3$—no result (*b*) $Hg_2(NO_3)_2$—warmed, gives a carmine colour

2. Mix the powder with conc. H_2SO_4 and rub with a crystal of $K_2Cr_2O_7$—purple colour changing to red indicates **Strychnine.** Confirm by adding a few c.c. of sulphovanadic acid to a little of the substance. Blue to violet colour, turning red on warming.

3. Fluorescence of the solution in dilute H_2SO_4 indicates **Quinine.** Confirm by

(*a*) Chlorine water followed by NH_4OH—green colour.

(*b*) Chlorine water, then a few drops $K_4Fe(CN)_6$, then a slight excess of ammonia—a deep red colour, quickly changing to dirty brown. Morphine interferes with this test.

4. To the solution in dilute H_2SO_4 add Cl water in excess, and then NH_4OH—yellowish white precipitate indicates **Cinchonine.** Confirm by the ferrocyanide reaction.

EXAMINATION OF COMPLEX CYANIDES

373. Such compounds as Prussian blue are insoluble in dilute mineral acids, and even when they are decomposed by caustic alkalis the complex anions remain in solution, and the metals which they contain are not detected by the usual analytical reactions. They may be examined as follows :

Before testing for metals, double cyanides should be destroyed and the cyanogen completely removed from the substance. Mix

a suitable quantity of the material with three times its bulk of a mixture of one part of ammonium nitrate and two of ammonium sulphate, and ignite in the fume chamber until the reaction is complete and all ammonium salts are volatilised. The cyanogen is oxidised to CO_2 and free nitrogen, while the metals, including those originally present in the anions, remain as sulphates or oxides. Dissolve the residue in dilute HCl, and examine for cations in the usual manner.

Barium or strontium will, of course, form insoluble sulphates, and will require fusion (364).

Mercury and arsenic are volatile and may be completely expelled during the ignition. They are, however, easily detected by the dry tests, which give conclusive evidence regarding these metals.

To detect the acids, boil a portion of the substance with sodium hydroxide and a little solid sodium carbonate, the latter being required to precipitate Pb, Zn or Al, since the hydroxides of these metals are soluble in caustic soda. The precipitate contains hydroxides or carbonates of most of the heavy metals present, and may be neglected. The filtrate contains the soluble sodium salts of ferrocyanic, ferricyanic and cobalticyanic acids and of thiocyanic acid. Acidify the filtrate with HCl, and add excess of $FeCl_3$. A precipitate of Prussian blue indicates hydroferrocyanic acid. Filter. A deep red colour, or even a red tinge, in the filtrate indicates thiocyanic acid. To test for hydroferricyanic acid, which is rapidly reduced in presence of alkali to hydroferrocyanic, allow the first few drops of the filtrate to fall into an acidified solution of $FeSO_4$. A deep blue precipitate of Turnbull's blue indicates the presence of hydroferricyanic acid. Confirm these by the reactions with $AgNO_3$.

Silver cobalticyanide, $Ag_3Co(CN)_6$, is white, insoluble in HNO_3, but, unlike $Ag_3Fe(CN)_6$, is soluble in ammonia.

Cobalticyanide gives a light blue precipitate with $CuSO_4$, insoluble in dilute HNO_3, but soluble in ammonia to form a deep blue solution.

Hydrocyanic acid in presence of all complex cyanides is detected by distilling with excess of $NaHCO_3$, which decomposes

cyanides only, the others being stable. The vapour is passed into $AgNO_3$ solution containing HNO_3, or into yellow ammonium sulphide solution. In the first case AgCN is precipitated. In the latter NH_4SCN and NH_4SH are formed, and on acidifying with HCl and boiling off H_2S, $FeCl_3$ forms the red $Fe(SCN)_3$.

Iodides interfere with the detection of thiocyanic acid, and must be removed. First distil off the HCN as just described, then precipitate the halides and HSCN by acidifying with HNO_3 and adding excess of $AgNO_3$. Wash the precipitate by decantation and shake with 6N ammonia (10 c.c. 0·880 ammonia to 25 c.c. water). AgI is left practically unaffected, while AgSCN, AgCl and most of the AgBr are dissolved. Filter and precipitate the silver with H_2S. Evaporate the filtrate, acidify with HCl and add $FeCl_3$ to test for HSCN.

DETECTION OF HALIDES AND NITRATES IN PRESENCE OF CYANIDES

The above cyanogen acids must be removed before testing for halogens. To do this, take a portion of the neutral solution prepared as directed in par. **354**, make slightly acid with dilute sulphuric acid, and add a solution of zinc sulphate so long as a precipitate forms. Cyanides and complex cyanides are precipitated as insoluble zinc salts, and halides may be detected in a portion of the filtrate by means of silver nitrate.

Another portion of the filtrate may be tested for nitrates (after removing iodides also if present, **343**), as the complex cyanides interfere also with the reactions for nitrate and nitrite.

REACTIONS OF SOME RARE ELEMENTS

374. Certain elements are of such rare occurrence that their compounds are necessarily omitted from the ordinary courses of practical training in chemistry. Some of these are of great interest. The discovery of indium and thallium gave convincing evidence of the value of the spectroscope in chemical investigation. The existence of several, such as gallium and germanium, was foretold by Mendeléeff, and their subsequent discovery played a notable part in the establishment of the periodic law during the later years of the nineteenth century. The marked relationship among the elements of Groups III, IV, VI, many of which are among the rare elements, illustrate the value and significance of that great generalisation.

The increasing use of compounds of rare elements in many manufactures and their occurrence as commercial products makes it desirable to give a brief account of the more important ones here.

375. Beryllium. Be. DRY REACTION. Beryllium compounds cannot be reduced on charcoal. Moistened with $Co(NO_3)_2$ and reheated, the residue is grey. The double fluoride, $KBeF_3$, obtained by fusing Be compounds with KHF_2, is soluble in water, while the corresponding compound of Al, to which Be bears the closest resemblance, is insoluble.

Beryllium forms only one oxide, BeO, a white powder melting at 2,450°, insoluble in water, soluble in acids to yield the only class of beryllium salts.

REACTIONS IN SOLUTION. $Be^{\cdot\cdot}$. Use the sulphate, $BeSO_4$.

1. H_2S gives no precipitate, while $(NH_4)_2S$ gives the white hydroxide.

2. **NaOH** or **NH_4OH** precipitates the white gelatinous hydroxide, $Be(OH)_2$, insoluble in ammonia, soluble in cold NaOH or KOH to form beryllate, Na_2BeO_2. The latter, unlike the aluminate, is hydrolysed by boiling, reprecipitating the hydroxide. $Be(OH)_2$ differs from $Al(OH)_3$ also in being soluble in 10 per cent. $NaHCO_3$ solution.

3. **Na_2CO_3** or **$(NH_4)_2CO_3$** gives a white basic carbonate, soluble in excess of either reagent and reprecipitated on boiling. The normal carbonate, $BeCO_3 . 4H_2O$, is obtained by passing CO_2 through a cold suspension of the precipitate.

4. **Ether** saturated with water and HCl dissolves $BeCl_2$; aluminium chloride remains as $AlCl_3 . 4H_2O$.

In the course of analysis beryllium appears with aluminium in Group III as the soluble beryllate Na_2BeO_2. This may be hydrolysed by boiling, $Be(OH)_2$ precipitating while $Al(ONa)_3$ remains in solution. It is better to acidify the solution with acetic acid, add ammonium acetate and an acetic acid solution of 8-hydroxyquinoline (oxine), which precipitates the Al completely as the oxine salt $Al(C_9H_6ON)_3$. This is filtered, the filtrate made alkaline with NH_4OH and boiled to precipitate $Be(OH)_2$.

376. Cerium. Ce. This is the most abundant metal of the rare cerite group, and except for lanthanum, the most basic. It is a grey metal resembling tin, may be cut with a knife, decomposes water slowly and forms two oxides. Cerous oxide, Ce_2O_3, forms colourless salts; ceric oxide, CeO_2, is more stable, and is amphoteric: the salts are orange to red in colour.

DRY REACTION. The borax bead in the oxidising flame is brown while hot, yellow to colourless on cooling, and colourless in the reducing flame.

REACTIONS IN SOLUTION. **Cerous salts. $Ce^{\cdots}$.** Use the nitrate, $Ce(NO_3)_3 . 6H_2O$, or other salt.

1. **HCl** and **H_2S** give no precipitates, the chloride being soluble and the sulphide not formed in solution.

2. **NaOH** or **KOH** precipitates the white hydroxide, $Ce(OH)_3$, even when tartaric or citric acid, etc., is present. **NH_4OH** or **$(NH_4)_2S$** gives the same precipitate, except in presence of these organic compounds. The hydroxide oxidises in air to $Ce(OH)_4$, the colour changing through blue-grey and violet to yellow.

3. **Na_2CO_3** or **$(NH_4)_2CO_3$** forms white, basic carbonates which become crystalline on standing, insoluble in excess. The carbonates, like the oxalates, are useful for fractional precipitation of the metals of the cerite group.

4. **$(NH_4)_2C_2O_4$ or oxalic acid** gives a white precipitate of cerous oxalate, $Ce_2(C_2O_4)_3$, insoluble in excess (cf. Th) and in dilute HCl.

5. **Oxidising agents** convert cerous hydroxide into yellow ceric hydroxide, $Ce(OH)_4$. **Chlorine** passed into an alkaline suspension of $Ce(OH)_3$ converts this into yellow $CeO_2 . 3H_2O$, soluble with excess of chlorine. **Bromine** has a similar oxidising effect, but does not dissolve the CeO_2. **H_2O_2** added to ammoniacal $Ce(OH)_3$ converts it into reddish-brown *perceric hydroxide*, $CeO_3 . aq$. This is unstable, and on boiling leaves yellow $Ce(OH)_4$.

Ceric salts. $Ce^{\cdots\cdot}$. Use the nitrate, $Ce(NO_3)_4$. All ceric salts are coloured yellow to red and orange, and the solutions are similarly coloured. They are used as oxidising agents like $KMnO_4$. Ceric salts are very easily reduced, even by hot HCl.

6. **KOH** or **NH_4OH** precipitates the yellow $Ce(OH)_4$, insoluble in excess, soluble in HNO_3 to form $Ce(NO_3)_4$, but reduced in contact with HCl :

$$2Ce(OH)_4 + 2Cl' + 8H^{\cdot} \rightarrow 2Ce^{\cdots} + Cl_2 + 8H_2O.$$

7. **Ferrous salts** are oxidised to ferric, the ceric salt being reduced to cerous :

$$Ce^{\cdots\cdot} + Fe^{\cdot\cdot} \rightarrow Ce^{\cdots} + Fe^{\cdots}.$$

8. **H_2O_2** behaves as with permanganate, reducing both itself and the ceric salt :

$$2Ce^{\cdots\cdot} + H_2O_2 \rightarrow 2Ce^{\cdots} + 2H^{\cdot} + O_2.$$

9. **$(NH_4)_2C_2O_4$ or oxalic acid** precipitates a yellowish oxalate, soluble in a large excess, and reduced on warming with complete precipitation of cerous oxalate, $Ce_2(C_2O_4)_3$. This on ignition leaves the oxide CeO_2.

10. **NH_4NO_3** in conc. HNO_3 forms a sparingly soluble double nitrate, $Ce(NH_4)_2(NO_3)_6H_2O$, less soluble in HNO_3 than the corresponding salts of other cerite metals.

377. Lanthanum. La. This metal closely resembles cerium in properties. It is of a white colour, and forms only one oxide, La_2O_3, the most basic of the group. In its action with water and CO_2 it behaves like lime, and unites with acids to form colourless salts.

REACTIONS IN SOLUTION. $La^{\cdots}$. The chloride or the nitrate, $La(NO_3)_3 6H_2O$, may be used; the sulphate, $La_2(SO_4)_3 9H_2O$, is sparingly soluble in water.

1. **H_2S** gives no precipitate.

2. **NaOH** or **KOH** forms the white hydroxide, $La(OH)_3$, slightly soluble in water, giving an alkaline solution: this decomposes ammonium salts, liberating NH_3, and absorbs CO_2 to form the carbonate.

3. **$(NH_4)_2CO_3$** produces a white precipitate of carbonate, slightly soluble in excess. From this solution a double lanthanum ammonium carbonate crystallises slowly.

4. **$(NH_4)_2C_2O_4$** or oxalic acid gives a white, crystalline precipitate of the oxalate, insoluble in excess of either reagent, soluble in mineral acids.

5. **NH_4OH** or **$(NH_4)_2S$** forms a white, basic salt, except in presence of tartaric acid. It is soluble in mineral acids.

6. **H_2SO_4** precipitates the sulphate, which is easily soluble in ice-cold water. On warming gradually to 32° pure lanthanum sulphate, $La_2(SO_4)_3 . 9H_2O$ separates almost completely.

7. **K_2SO_4** forms the white crystalline double salt, potassium dilanthanum hexasulphate, $La_2(SO_4)_3 3K_2SO_4$, which is anhydrous and insoluble in K_2SO_4 solution.

378. Thallium. Tl. DRY REACTION. Thallium compounds colour the flame green, similar to but less yellow than the barium colour. The spectroscope should be used for this test.

Thallium forms two basic oxides: thallous oxide, Tl_2O, soluble in water and alcohol giving alkaline solutions; and thallic oxide, Tl_2O_3. There are two corresponding classes of salts.

REACTIONS IN SOLUTION. $Tl^{\cdot}$. Use thallous sulphate, Tl_2SO_4.

1. **HCl, HBr, HI,** or their alkali salts, precipitate respectively white TlCl, sparingly soluble in cold water, more soluble in hot water (cf. lead); pale yellow TlBr, less soluble, and yellow TlI, practically insoluble in cold water. The fluoride is soluble.

2. **H_2S** in neutral solution precipitates black thallous sulphide, Tl_2S, soluble in mineral acids, insoluble in acetic acid or alkali sulphides. $(NH_4)_2S$ precipitates it completely. It oxidises in air

to the sulphate, Tl_2SO_4, which is very stable and vaporises without decomposition at high temperatures.

3. **NH_4OH** or **NaOH** gives no precipitate.

4. **$(NH_4)_2CO_3$** or **Na_2CO_3** precipitates the carbonate, Tl_2CO_3, from concentrated solutions : its solubility is about five per cent. at room temperature.

5. **K_2CrO_4** forms yellow Tl_2CrO_4, insoluble in dilute HNO_3 or H_2SO_4. It is about three times more soluble than $PbCrO_4$.

6. **H_2PtCl_6** gives a yellow salt similar to that of potassium, but very slightly soluble in water.

7. **$Na_3[Co(NO_2)_6]$** forms a bright red thallium cobaltinitrite, $Tl_3[Co(NO_2)_6]$.

$Tl^{\cdots}$. The chloride and chromate are soluble ; the sulphate, $Tl_2(SO_4)_3 7H_2O$, and nitrate, $Tl(NO_3)_3 4H_2O$, are hydrolysed by water. The bromide and iodide are less stable than the chloride, TlI_3 acting as a mixture with $TlI \cdot I_2$ analogous to $KI \cdot I_2$.

8. **KI** precipitates thallous iodide together with free iodine :

$$Tl^{\cdots} + 3I' \rightarrow TlI + I_2.$$

9. **NH_4OH** or **NaOH** gives a brown thallic hydroxide, $Tl(OH)_3$ or $TlO(OH)$, insoluble in excess of alkali. It loses all the water at 120°, leaving Tl_2O_3.

10. **H_2S** reduces thallic to thallous salts, with separation of sulphur, and alkali sulphide precipitates thallous sulphide, Tl_2S.

379. **Indium. In.** Dry Reactions. 1. Heated on charcoal, indium salts form a lustrous film on the surface.

2. The Bunsen flame is coloured bluish violet. The spectrum contains several blue (indigo) lines.

Reactions in Solution. $In^{\cdots}$. Use the chloride, nitrate or sulphate, which are all soluble in water. There are three chlorides, $InCl$, $InCl_2$ and $InCl_3$, but only the salts of the trivalent ion are stable in water, the others decomposing into $InCl_3$ and the metal.

3. **H_2S** in slightly acid solution precipitates a yellow sulphide, In_2S_3 :

$$2In^{\cdots} + 3H_2S \rightarrow In_2S_3 + 6H^{\cdot}.$$

Like CdS, this does not form in 0·5 N. HCl. When boiled with

yellow $(NH_4)_2S_x$ the yellow In_2S_3 changes to a white sulphide of uncertain composition, possibly the complex $(NH_4)_2[In_2S_4]$.

4. **NH_4OH** or **NaOH** gives white, gelatinous $In(OH)_3$, like $Al(OH)_3$ in appearance, and like it also soluble in excess of NaOH, but not in NH_4OH. This fact serves for the separation of indium from zinc and cadmium, with which it occurs. Indium is estimated as hydroxide, which on ignition leaves the oxide In_2O_3.

5. **$(NH_4)_2CO_3$** or **Na_2CO_3** precipitates white $In_2(CO_3)_3$, soluble in excess of ammonium carbonate, but reprecipitated on boiling.

6. **RbCl** added to a solution of $In(OH)_3$ in concentrated HCl forms rubidium hexachloroindate, $3RbCl \cdot InCl_3$. The colourless octahedra crystallise so readily that the reaction is recommended as a microchemical test.

380. **Gallium. Ga.** Dry Reaction. The flame colour is violet, the spectrum consisting chiefly of two brilliant violet lines between the G and H lines.

Reactions in Solution. **$Ga^{...}$**. Salts of the bivalent gallous ion, $Ga^{..}$, are unstable and readily form gallic salts which resemble the aluminium salts. Gallic oxide, although amphoteric, is more basic than Al_2O_3.

1. **HCl** dissolves the metal forming the soluble chloride, $GaCl_3$, and liberating hydrogen. The chloride is obtained also by heating the metal in HCl or Cl_2.

2. **H_2S,** or **$(NH_4)_2S$,** usually causes no precipitate, but gallium sulphide may come down with others in the copper group if only slightly acid, or completely with others in the zinc group as white Ga_2S_3.

3. **NH_4OH** or **NaOH** forms a white gelatinous precipitate of gallium hydroxide, $Ga(OH)_3$, soluble in excess of either reagent and reprecipitated on boiling the ammoniacal solution. When ignited the hydroxide leaves Ga_2O_3. This method is used for the estimation. The metal dissolves in NaOH solution liberating hydrogen.

4. **$(NH_4)_2CO_3$** or **Na_2CO_3** produces a white, basic carbonate, soluble in excess of ammonium carbonate.

5. **The sulphate, $Ga_2(SO_4)_3$,** forms a sparingly soluble basic sulphate on boiling its aqueous solution.

6. $K_4[Fe(CN)_6]$ gives a white or bluish-white precipitate of $Ga_4[Fe(CN)_6]_3$, insoluble in dilute HCl. This is a delicate test for gallium.

381. Germanium. Ge. DRY REACTION. Heated on charcoal, germanium compounds are easily reduced to the greyish white metal, which is crystalline, brittle and easily oxidised.

The dioxide, GeO_2, is a white powder slightly soluble in water (about 1 per cent. at 100°), forming germanic acid, H_2GeO_3. This corresponds with H_2SnO_3 and forms salts with both acids and bases.

REACTIONS IN SOLUTION. $Ge^{....}$. Use a solution of the oxide, GeO_2.

1. **HCl** and other acids cause no precipitate. The chloride, $GeCl_4$, a colourless liquid of b.p. 75°, is obtained by passing dry chlorine over the metal, and is hydrolysed by water (cf. $SiCl_4$, $SnCl_4$). The bromide, $GeBr_4$, b.p. 186°, results on distilling germanium compounds with concentrated HBr. The dichloride, $GeCl_2$, is also a colourless liquid, fuming in air, and like $SnCl_2$ is a strong reducing agent.

2. H_2S passed into the aqueous solution of the oxide forms a white precipitate of sulphide, GeS_2, sparingly soluble in water and hydrolysed by it, H_2S being evolved. The sulphide is soluble in ammonium or alkali sulphides or hydroxides, and reprecipitated with acid. It is oxidised by air or HNO_3 to the oxide GeO_2.

3. **HF** converts the oxide or the sulphide into H_2GeF_6; from the solution of this K_2CO_3 precipitates, on warming, the sparingly soluble greyish-white potassium salt, K_2GeF_6.

382. Titanium. Ti. This metal is similar to iron in appearance. It burns brightly in air, forming the white oxide TiO_2, and also a nitride. It occurs chiefly as the dioxide in several forms, and in combination as titanates of iron, calcium and other metals. The salts of TiO_2 are colourless and are those most commonly met with. Titanous oxide, Ti_2O_3, and its salts give violet solutions and are strong reducing agents. They behave towards common reagents like the salts of aluminium and iron.

DRY REACTION. The microcosmic bead is colourless in the oxidising flame, and in the reducing flame yellow when hot and violet when cold, especially if some $SnCl_2$ is added.

REACTIONS IN SOLUTION. $Ti^{\cdot\cdot\cdot\cdot}$. Use the sulphate, $Ti(SO_4)_2$.

1. **Water** hydrolyses all titanic salts on boiling, *m*-titanic acid being precipitated (cf. tin). Tartaric and citric acids tend to prevent this:

$$Ti^{\cdot\cdot\cdot\cdot} + 3H_2O \rightarrow H_2TiO_3 + 4H^{\cdot}.$$

2. **NaOH, NH_4OH,** or the sulphides, in the cold form the white, gelatinous *o*-titanic acid, H_4TiO_4, almost insoluble in excess, soluble in mineral acids. In hot solutions these reagents or alkali acetates or thiosulphates precipitate metatitanic acid, in the last case mixed with sulphur:

$$Ti^{\cdot\cdot\cdot\cdot} + 2S_2O_3'' + H_2O \rightarrow H_2TiO_3 + 2S + 2SO_2.$$

3. **Na_2HPO_4** forms a white precipitate of $Ti(HPO_4)_2$, insoluble in dilute H_2SO_4. H_2O_2 prevents this by oxidising the titanium.

4. H_2O_2 gives an orange-red coloration due to TiO_3 in slightly acid solution. In very dilute solutions the colour is yellow This is a delicate test for titanium, but fluoride and phosphate tend to destroy it.

5. **Zinc** or **tin,** in HCl solution of a titanic salt, causes reduction to the violet titanous salt. SO_2 or H_2S do not effect this reduction.

6. **Cupferron** gives a flocculent yellow precipitate in acid solution, of the composition $Ti(C_6H_5NO \,.\, NO)_4$.

383. **Zirconium. Zr.** The powdered metal burns in air to form the only important oxide, ZrO_2. This occurs in union with silica in the mineral zircon, $ZrSiO_4$, from which zirconium compounds are obtained by fusion with alkali carbonates.

REACTIONS IN SOLUTION. $Zr^{\cdot\cdot\cdot\cdot}$. Use the nitrate, $Zr(NO_3)_4$, or the chloride, or a freshly prepared solution of zirconyl chloride, $ZrOCl_2$.

1. **NaOH, NH_4OH** or the sulphides precipitate the white hydroxide $Zr(OH)_4$, insoluble in excess, soluble in cold HCl. Boiling renders it more difficult to dissolve.

2. **Na_2CO_3** or **$(NH_4)_2CO_3$** gives white basic carbonates soluble in excess of ammonium carbonate, reprecipitated on boiling.

3. **Na_2HPO_4** forms the white phosphate, $Zr(HPO_4)_2$, insoluble in 20 per cent. H_2SO_4. H_2O_2 does not interfere (cf. titanium).

4. **$(NH_4)_2C_2O_4$** or oxalic acid precipitates white zirconium oxalate, $Zr(C_2O_4)_2$, sparingly soluble in dilute HCl; soluble in excess of ammonium oxalate and not reprecipitated by HCl (cf. thorium).

384. Thorium. Th. The most important compounds of thorium are those based on the dioxide, ThO_2, which occurs in thorite, $ThSiO_4$. The metal is not affected by air at room temperature, but on heating it burns to the dioxide. ThO_2 is also obtained by igniting the nitrate, $Th(NO_3)_4$, by which process it is introduced into gas mantles. With 1–2 per cent. of CeO_2 the incandescent glow is much brighter.

REACTIONS IN SOLUTION. **$Th^{....}$**. Use the nitrate, $Th(NO_3)_4$, or sulphate, $Th(SO_4)_2$.

1. **NaOH**, **NH_4OH** or the sulphides precipitate white thorium hydroxide, $Th(OH)_4$, insoluble in excess, easily soluble in acids when freshly precipitated. When ignited the hydroxide leaves ThO_2, very difficult to dissolve in acids.

2. **Na_2CO_3** or **$(NH_4)_2CO_3$** forms the white carbonate, soluble in excess and not reprecipitated. Basic carbonates form on boiling, but redissolve on cooling.

3. **Na_2HPO_4** gives no precipitate, but sodium hypophosphate, $NaHPO_3$, forms white thorium hypophosphate, ThP_2O_6, on boiling, insoluble in mineral acids.

4. **$(NH_4)_2C_2O_4$** or oxalic acid throws out the white, crystalline oxalate, $Th(C_2O_4)_2 \cdot 6H_2O$, soluble in excess of ammonium oxalate, reprecipitated on addition of HCl.

5. ***m*-Nitrobenzoic acid** precipitates $Th(NO_2C_6H_4COO)_4$, a white salt, from neutral solutions at 70°–80° (difference from cerium).

6. **KF** or **HF** gives a bulky white precipitate of thorium fluoride, ThF_4, which becomes compact on standing (distinction and separation from Al, Ti, Be).

385. Vanadium. V. Vanadium forms five oxides, corresponding to those of nitrogen. The three lowest oxides are basic and their solutions have strong reducing properties. The tetroxide, vanadyl oxide, V_2O_4, is a blue powder soluble both in acids and alkalis. The pentoxide, V_2O_5, forms orange-red crystals. It is the most important oxide. All the lower oxides may be converted into V_2O_5 or its salts by boiling with HNO_3 or fusing with fusion mixture and KNO_3. It is the analogue of P_2O_5 and As_2O_5, with which it forms series of complex acids, salts of which occur among minerals. The oxychloride, $VOCl_3$, b.p. 120°, is the analogue of $POCl_3$. Vanadic oxide, V_2O_5, like P_2O_5, forms three types of acid, of which the meta- is the most stable. The ortho-salts are hydrolysed in solution :

$$2Na_3VO_4 \xrightarrow[\text{cold}]{H_2O} Na_4V_2O_7\ (+2NaOH) \xrightarrow[\text{hot}]{H_2O} 2NaVO_3\ (+2NaOH).$$

Polyvanadic acids such as tetra- and hexa-vanadic acids are formed by the action of mineral acids on the above salts. They have intense red or orange colours.

DRY REACTION. The borax bead is colourless in the oxidising flame unless there is much vanadium present, in which case the bead is yellow, becoming green in the reducing flame.

REACTIONS IN SOLUTION. **Vanadyl salts, $V_2O_2^{\cdots\cdot}$, and vanadic salts, $V^{\cdots\cdot\cdot}$.** The oxide V_2O_4 dissolves in concentrated H_2SO_4 to form the blue divanadyl sulphate, $V_2O_2(SO_4)_2$. Sodium meta-vanadate, $NaVO_3$, is easily soluble.

1. **H_2S** gives no sulphide in acid solutions of either type, but reduces vanadic acid to blue vanadyl salt. This change is effected also by SO_2 and other reducing agents, and serves for the detection of vanadium. The extent of the reduction can be determined by reoxidation with standard $KMnO_4$ solution.

2. **$(NH_4)_2S$** produces no precipitate, but forms red-brown thio-salts. On acidifying this solution the black sulphide V_2S_5 is partially precipitated, and the solution is of a blue colour.

3. **NH_4OH** precipitates grey-white hypovanadic acid from solutions of vanadyl salts :

$$V_2O_2^{\cdots\cdot} + 4OH' \rightarrow V_2O_2(OH)_4.$$

The acid is soluble in excess of ammonia, but in presence of cations like $Fe^{\cdots}$, $Al^{\cdots}$ or $Ba^{\cdot\cdot}$ the precipitation is complete. Vanadic acid in presence of ammonia precipitates $Fe^{\cdots}$, $Al^{\cdots}$, $UO_2^{\cdot\cdot}$, $Ba^{\cdot\cdot}$ as vanadates, corresponding with the phosphates.

4. **Oxidising agents** such as bromine water or Na_2O_2 convert the blue divanadyl salts into vanadic acid or its salts, which are colourless or pale yellow :

$$V_2O_2^{\cdots\cdot} + Na_2O_2 + 8OH' \rightarrow 2VO_4''' + 2Na^{\cdot} + 4H_2O.$$

In presence of alkali this reaction serves to separate V, with Cr, Al, Zn, which form soluble alkali salts, from the insoluble hydroxides of $Fe^{\cdots}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$ and $Mn^{\cdots}$ (359).

5. H_2O_2 added carefully to an acid solution of vanadic acid forms reddish-brown pervanadic acid, HVO_4, insoluble in ether. Excess of H_2O_2 must be avoided.

6. **8-Hydroxyquinoline**, in 2·5 per cent. solution, added to a vanadate solution containing acetic acid, precipitates the yellow salt $(C_9H_6NOH)_2H_2V_4O_{11}$. This is soluble in chloroform, to which it gives a reddish-violet colour. Small quantities of vanadium may thus be detected and separated from chromium.

386. **Molybdenum. Mo.** This silver-white metal forms four oxides ; MoO, Mo_2O_3 and MoO_2 are basic, and the acid anhydride, MoO_3, is a white crystalline powder soluble in NH_4OH or alkalis to form molybdates. The metal is used with tungsten in lamp filaments, for thermocouples and electric resistances, and in many alloys, ferromolybdenum and molybdenum steel.

Dry Reactions. 1. Heated on charcoal, molybdates are reduced to greyish metal with a white encrustation of MoO_3.

2. A metaphosphate bead in the oxidising flame is coloured brown to yellow according to concentration. On cooling it becomes greenish and finally colourless. In the reducing flame the bead is brown when hot and green on cooling.

Reactions in Solution. MoO_4''. Use ammonium molybdate, $(NH_4)_6Mo_7O_{24}4H_2O$, the paramolybdate, formed by evaporating a solution of MoO_3 in ammonia. The ammonium molybdates are the most important salts. Salts of the lower oxides, with

valencies of 2, 3, 4 and 5 are not important. They are formed by reducing the molybdates in various ways.

3. **Concentrated H_2SO_4** containing a trace of Mo acquires an intense blue colour on evaporating nearly to dryness. This forms a delicate test for Mo compounds in the absence of Sb, Sn and some other metals.

4. **HCl** and other acids precipitate white molybdic acid, H_2MoO_4, soluble in excess of acid or in alkalis.

5. **H_2S** and other reducing agents like $FeSO_4$, $SnCl_2$, Zn, first reduce the acid solution, giving colours intensely blue, then green, changing to brown. This is one of the most characteristic tests for molybdenum. Excess of H_2S slowly precipitates the brown sulphide, MoS_3. Complete precipitation requires pressure and is most rapid at 80–90°. The sulphide dissolves in alkalis or $(NH_4)_2S$ forming brown thiomolybdates, $(NH_4)_2MoS_4$, from which acids reprecipitate MoS_3. The sulphide is oxidised in air or with HNO_3, forming MoO_3.

6. **Na_2HPO_4** in presence of HNO_3 forms yellow ammonium phosphomolybdate (see phosphoric acid, 344, 3).

7. **KSCN** gives no precipitate with molybdates, but if the acid solution is treated with zinc the Mo is reduced to trivalent ion and a blood-red colour is produced due to $K_3[Mo(SCN)_6]$, soluble in ether. The colour is destroyed by H_2O_2. Phosphoric acid does not interfere with the reaction, as it does in the case of iron.

8. **$K_4Fe(CN)_6$** precipitates a brown ferrocyanide, $Mo_2[Fe(CN)_6]_2$, insoluble in dilute mineral acids, easily soluble in NaOH or NH_4OH (diff. from VO_2 and Cu ferrocyanides).

9. **Lead acetate** precipitates from acetic acid solutions heavy white lead molybdate, soluble in dilute HNO_3.

10. **$Hg_2(NO_3)_2$** gives a yellow mercurous molybdate, soluble in HNO_3. On ignition it leaves the oxide, MoO_3, and may be used for the estimation of Mo (cf. chromium).

387. Tungsten. W. Tungsten compounds closely resemble those of molybdenum. The iron-grey metal in powder form is very hard and brittle, but when pure it compares with gold in ductility. Like molybdenum it forms several oxides and derived

compounds in which the valency of the element varies from 2 to 6. The lower forms are unstable and unimportant. There is an unstable dioxide WO_2, a brown powder, and the stable yellow acid anhydride, WO_3, which, although practically insoluble in water, unites with alkalis to form soluble tungstates, the most important compounds of tungsten. Many complex acids and mineral compounds are known, in which WO_3 is united with oxides of B, P, V, As, Sb, Si, etc. The metal is used in lamp filaments, for alloys and in steel.

Dry Reaction. The microcosmic bead is colourless or pale yellow in the oxidising flame, and in the reducing flame blue, turning blood-red on adding $FeSO_4$.

Reactions in Solution. WO_4''. Use sodium tungstate, $Na_2WO_4 . 2H_2O$.

1. **HCl** and other acids in the cold, precipitate white hydrated tungstic acid, $H_2WO_4 . H_2O$, which on boiling forms the yellow anhydrous acid, insoluble in dilute HCl.

2. **H_2S** gives no sulphide in acid solution.

3. **$(NH_4)_2S$** forms no precipitate until the solution is acidified, when the brown trisulphide, WS_3, is thrown out. This is insoluble in dilute HCl, but soluble in ammonium sulphide, forming thiotungstate, $(NH_4)_2WS_4$.

4. **Phosphoric acid** gives a white precipitate of phosphotungstic acid, $H_3[PO_4 . 12WO_3]5H_2O$, soluble in excess of H_3PO_4.

5. **Zinc** and dilute HCl, or $SnCl_2$, reduces tungstates (H_2WO_4) to a beautiful blue colour or precipitate, due to the formation of WCl_5. $FeSO_4$ gives a brown precipitate, but no blue compound (cf. Mo).

388. **Uranium. U.** The pure metal is white, and tarnishes easily in moist air. It decomposes water slowly at room temperature, more rapidly on boiling. It dissolves in dilute HCl and H_2SO_4 liberating hydrogen and forming quadrivalent salts. In powder form it burns in oxygen at 170°. It gives several series of compounds in which its valency varies from 2 to 6 and perhaps 8. These are similar to the corresponding series of Mo and W compounds. There are three well-defined oxides: the dark-brown dioxide UO_2, the base of the unstable uranous salts; the

trioxide, UO_3, brick-red in colour, obtained by heating ammonium uranate, $(NH_4)_2U_2O_7$, at 300°; and U_3O_8, which is possibly a mixture of the other two. In accord with the position of U as the heaviest element of Group VI, the acidic properties of UO_3 are less pronounced than those of WO_3 and MoO_3, and the uranyl salts of the hydroxide $UO_2(OH)_2$ are the most important compounds. The metal is used to some extent in the manufacture of high-speed steels.

Dry Reaction. The borax bead is yellow in the oxidising flame and green in the reducing flame.

Reactions in Solution. $UO_2^{\cdot\cdot}$. Use uranyl nitrate or acetate, $UO_2(NO_3)_2 . 6H_2O$ or $UO_2(C_2H_3O_2)_2 2H_2O$. The chloride also is soluble. The salts are yellow or greenish-yellow.

1. H_2S gives no precipitate, the sulphide being soluble in dilute acids.

2. **NaOH** or NH_4OH precipitates a yellow, insoluble uranate, analogous to dichromates or pyrosulphates:

$$2UO_2Cl_2 + 6NH_4OH \rightarrow (NH_4)_2U_2O_7 + 2NH_4Cl + 3H_2O.$$

These dissolve in ammonium carbonate forming complex salts, $(NH_4)_4[UO_2(CO_3)_3]$.

3. Na_2CO_3 forms a similar complex salt, slightly soluble in water, but precipitated from concentrated solutions as sodium uranyl carbonate, $Na_4[UO_2(CO_3)_3]$. $BaCO_3$ precipitates uranyl salts completely as $Ba_2[UO_2(CO_3)_3]$.

4. $(NH_4)_2S$ gives a brown precipitate of uranyl sulphide, UO_2S, soluble in dilute acids, or in ammonium carbonate to form the double uranyl carbonate. In presence of alkali carbonates, therefore, neither the alkali hydroxides nor their sulphides precipitate uranium.

5. Na_2HPO_4 forms a pale yellow phosphate, UO_2HPO_4. In presence of ammonium acetate or hydroxide the uranium is completely precipitated as uranyl ammonium phosphate,

$$UO_2NH_4PO_4 . 6H_2O,$$

corresponding with the Mg and Be salts, and like them decomposed on ignition with formation of pyrophosphate, $(UO_2)_2P_2O_7$.

6. **$K_4Fe(CN)_6$** gives a brown coloration or precipitate of uranyl ferrocyanide, $(UO_2)_2[Fe(CN)_6]$, soluble in acetic acid. This is a very delicate test.

7. **Zinc** in dilute acid reduces uranyl salts to green uranous salts.

389. Selenium. Se. Selenium and tellurium are the analogues of sulphur, and in their chemical relationships are much more acidic than the metals just described, which appear in the *a* division of the same periodic group. Selenium is very similar to sulphur. It burns to the dioxide, SeO_2, which dissolves in hot water to form crystallisable selenious acid, H_2SeO_3. Selenites are the most commonly occurring compounds, and these may be oxidised to selenates.

DRY REACTIONS. 1. Heated on charcoal with Na_2CO_3, selenium compounds emit an odour of decaying radish. When moistened with HCl the residue evolves H_2Se, which has an offensive smell. On a silver coin a black stain of selenide, Ag_2Se, is formed.

2. Selenium dissolves in concentrated H_2SO_4 giving a green solution due to $SeSO_3$. On dilution the colour disappears and Se is precipitated as a red powder, β-Se, which changes slowly to the more stable dark-grey γ-form.

$$SeSO_3 + H_2O \rightarrow Se + H_2SO_4.$$

REACTIONS IN SOLUTION. **SeO_3''.** Use selenious acid, H_2SeO_3.

3. **H_2S** gives a yellow precipitate containing Se and S, the Se becoming red on heating; both dissolve in ammonium sulphide:

$$H_2SeO_3 + 2H_2S \rightarrow Se + 2S + 3H_2O.$$

4. **Reducing agents,** SO_2, $SnCl_2$, Zn, Fe, HI, etc., all give red selenium more or less readily, especially on warming. The red Se slowly darkens to grey or black. A spot test may be made with HI solution and a drop of the selenious solution on filter paper. A reddish-brown spot is produced, the red Se remaining after addition of $Na_2S_2O_3$.

5. **$BaCl_2$, $CuSO_4$,** and other salts give precipitates resembling the corresponding sulphites, decomposed by dilute acids.

SeO_4''. Use potassium selenate, K_2SeO_4.

6. H_2S gives no precipitate in the cold, but on boiling the selenic acid is reduced to selenious acid, which is then decomposed as above. SO_2 does not reduce H_2SeO_4.

7. $BaCl_2$ precipitates white $BaSeO_4$, insoluble in dilute HCl, reduced by boiling with concentrated HCl :

$$BaSeO_4 + 4HCl \rightarrow H_2SeO_3 + BaCl_2 + Cl_2 + H_2O.$$

390. **Tellurium. Te.** Tellurium is less common than selenium, usually occurring as tellurides of silver and gold, less frequently with lead, mercury, etc. The element is silver-white, crystalline, brittle, stable in air or oxygen ; but on heating it burns with a bluish-green flame forming the dioxide TeO_2. The compounds resemble those of S and Se, but Te is more metallic.

Dry Reactions. 1. Fusion of tellurium compounds with Na_2CO_3 on charcoal yields sodium telluride, Na_2Te, which when moistened on a silver coin forms a black stain of silver telluride, Ag_2Te.

2. Free tellurium is obtained by heating any telluride on asbestos in the reducing flame, and may be collected as a black film on the bottom of a test-tube filled with cold water. This film dissolves in conc. H_2SO_4 giving a red solution of $TeSO_3$ ($SeSO_3$ is green). On dilution with water Te is precipitated as a grey-black powder .

$$TeSO_3 + H_2O \rightarrow Te + H_2SO_4.$$

3. Fused with KCN, tellurium compounds form K_2Te, which dissolves in water, forming a red solution. On passing air through this solution black Te is precipitated :

$$2K_2Te + O_2 + 2H_2O \rightarrow 2Te + 4KOH.$$

Selenium under the same treatment forms the soluble selenocyanide, KSeCN, which is decomposed, not by oxygen, but by dilute HCl :

$$KSeCN + HCl \rightarrow Se + KCl + HCN.$$

This reaction serves for the separation of Se and Te.

Reactions in Solution. TeO_3''. Use potassium tellurite, K_2TeO_3.

1. **HCl** gives a white precipitate of tellurous acid, H_2TeO_3, except in very dilute solutions.

2. **H_2S** causes precipitation of brown tellurium sulphide, TeS_2, insoluble in HCl, soluble in $(NH_4)_2S$. It decomposes easily into tellurium and sulphur.

3. **$SnCl_2$, zinc, SO_2** and some other reducing agents precipitate black Te. $FeSO_4$ or HI do not reduce either tellurous or telluric acid.

TeO_4''. Use potassium tellurate, K_2TeO_4.

1. **HCl** does not precipitate telluric acid, but on boiling the telluric acid is reduced to tellurous acid, which is precipitated; chlorine is evolved.

2. **H_2S** causes no precipitation in the cold, and the sulphides of Group II can be removed in the cold. On heating, tellurous acid is formed and converted into TeS_2 as above.

3. **Barium,** copper and other salts are in general similar to those of sulphuric and selenic acids, but $BaTeO_4$ is only precipitated from concentrated solutions, and is reduced on boiling with conc. HCl:

$$BaTeO_4 + 4HCl \rightarrow H_2TeO_3 + BaCl_2 + Cl_2 + H_2O.$$

391. Gold. Au. There are two oxides: aurous oxide, Au_2O, and auric oxide, Au_2O_3. Both are very unstable and decompose when slightly heated, leaving the metal. The salts also are unstable, and only the auric salts are important. Auric chloride is the most stable of these, and when gently heated it liberates chlorine, giving first aurous chloride and then gold. Aurous chloride is insoluble in water, but when boiled in water it reverts to auric chloride and the metal:

$$3AuCl \rightarrow AuCl_3 + 2Au.$$

DRY REACTION. All gold compounds are easily reduced on charcoal, especially in presence of an alkaline flux, and form the yellow, malleable metal.

REACTIONS IN SOLUTION. **Au'''.** Use gold chloride, $AuCl_3$.

1. **HCl** unites with gold chloride to form the complex chloro-auric acid, $HAuCl_4$, which forms many well-crystallised salts, especially with organic bases.

2. **H_2S** in cold, slightly acid solutions precipitates the black disulphide, Au_2S_2, soluble in aqua regia or in alkali sulphides or polysulphides to form thiosalts, as $KAuS_2$. Acids reprecipitate the sulphide.

3. **NaOH** added to a concentrated solution forms the reddish-brown hydroxide, soluble in excess :

$$AuCl_4' + 3OH' \rightarrow Au(OH)_3 + 4Cl',$$
$$Au(OH)_3 + OH' \rightarrow AuO_2' + 2H_2O.$$

4. **$SnCl_2$** reduces gold salts to the metal, which forms a brown suspension of very fine powder. In very dilute solutions **purple of Cassius** is produced, consisting of stannic hydroxide with adsorbed colloidal gold :

$$2Au''' + 3Sn'' \rightarrow 3Sn'''' + 2Au.$$

Other reducing agents, including oxalic acid, $FeSO_4$, SO_2, zinc, and alkaline H_2O_2, reduce gold salts to the metal.

5. **KI** precipitates the metal from alkaline solutions ($KAuO_2$), giving a brown or purple suspension :

$$2AuO_2' + 6I' + 4H_2O \rightarrow 2Au + 8OH' + 3I_2.$$

6. **Benzidine** (0·05 per cent. in 10 per cent. acetic acid) is oxidised by auric salts to a blue dye. Adjacent drops on filter paper or mixed on a tile give the blue colour. This is a very delicate test for gold in the absence of other oxidising agents (Mn salts, PbO_2, etc.).

392. Platinum. Pt. DRY REACTION. Compounds of platinum heated on charcoal leave the dark-grey spongy metal. This can be rubbed to a lustrous film on glass, and is unaffected by conc. HNO_3 (cf. Pb, Ag, Sn, etc.).

REACTIONS IN SOLUTION. **Pt''''**. Use chloroplatinic acid, $H_2PtCl_6 . 6H_2O$.

1. **H_2S** forms the dark-brown sulphide, PtS_2, slowly in the cold, more rapidly on warming. The sulphide is insoluble in acids, soluble in aqua regia and in alkali polysulphides, with which it forms thiosalts that are decomposed on acidifying.

2. **KCl** and **NH_4Cl** in concentrated solutions form sparingly soluble double salts, $K_2[PtCl_6]$ and $(NH_4)_2[PtCl_6]$. These separate as yellow crystalline precipitates, insoluble in alcohol.

3. **KI** causes a brown coloration owing to the formation of the complex $[PtI_6]''$, less ionised than $[PtCl_6]''$.

4. **Formaldehyde** precipitates the metal as *platinum black* from alkaline solutions. In this form the metal has remarkable catalytic power.

5. **Carbon monoxide** reduces platinum solutions, in presence of sodium acetate, to a beautiful red colloidal solution. This slowly precipitates as a black powder.

Ferrous salts, zinc, magnesium and other metals, formic acid and many other reducing agents precipitate the metal as a black powder. Oxalic acid precipitates gold (brown powder), but not platinum or other Group II metals.

6. **$SnCl_2$** reduces H_2PtCl_6 to chloroplatinous acid only, not to the metal:

$$[PtCl_6]'' + Sn^{..} \rightarrow Sn^{....} + 2Cl' + [PtCl_4]''.$$

393. **Rubidium. Rb.** The flame coloration is reddish-violet, the spectrum having double lines in both red and violet.

REACTIONS IN SOLUTION. **$Rb^{\cdot}$**. Use the chloride, RbCl.

1. **H_2PtCl_6** forms a yellow crystalline precipitate of Rb_2PtCl_6, similar to but less soluble than the potassium salt.

2. **Tartaric acid** gives from concentrated solutions a white crystalline precipitate of the bitartrate, more soluble than the corresponding potassium salt.

3. **$Na_3[Co(NO_2)_6]$** precipitates a yellow crystalline double salt, $Rb_2Na[Co(NO_2)_6]$, which on gentle ignition leaves a residue of Co_3O_4, together with soluble nitrites of sodium and rubidium. The compound is less soluble than the potassium salt.

4. **$Bi(NO_3)_3$** in concentrated solution with a large amount of $NaNO_2$ forms a yellow crystalline double nitrite, $Rb_2NaBi(NO_2)_6$.

Many other sparingly soluble double salts are known, by means of which Rb and Cs may be identified and separated from the other alkalis. Rubidium salts are employed as reagents in microchemistry.

394. Caesium. Cs. Caesium salts give a reddish-violet flame coloration, similar to those of Rb and K salts. In the spectrum there is a bright blue double line and subordinate lines in the red and orange.

REACTIONS IN SOLUTION. **$Cs^{\cdot}$.** Use the chloride, CsCl.

The same reactions may be applied to caesium as are used for rubidium salts. The precipitates obtained are similar in colour, appearance and crystalline form. The differences to be observed are mainly in solubility, the caesium salts being generally less soluble than those of rubidium, and these again less soluble than the potassium salts, although in some cases, as the bitartrates, the order is reversed. Caesium platinichloride, Cs_2PtCl_6, is less soluble than any other platinichloride, and although it is difficult to separate from the others, the metal is best estimated in this form.

395. Separation of the rare elements. A complete scheme for the separation of the elements just considered is unnecessary for the purpose of this book, but some indication may be given of the relation of these elements to those commonly met with in analysis, and the following brief notes may be useful.

GROUP I. Thallium is precipitated as TlCl and dissolves in hot water with $PbCl_2$. Separate the lead as $PbSO_4$, and to the filtrate add KI to form TlI (and some PbI_2). The PbI_2 is soluble in $Na_2S_2O_3$; TlI is insoluble.

Tungsten is precipitated from orthotungstates as H_2WO_4 insoluble in HCl. Boil to hydrolyse metatungstates and complete the precipitation of H_2WO_4. This dissolves in NH_4OH, together with AgCl. Neutralise most of the ammonia, keeping the AgCl in solution, add KI in excess, filter the AgI and concentrate the filtrate. Acidify with HCl and add zinc or $SnCl_2$: a blue colour indicates tungsten.

GROUP II. Selenium and tellurium are precipitated by H_2S, Se red in the cold, black in hot solutions, and Te black. They are mixed with sulphur, both soluble in $(NH_4)_2S_x$ and reprecipitated along with As_2S_3, etc. They may be separated with KCN, and are best identified by the H_2SO_4 tests.

Molybdenum, platinum and gold sulphides dissolve in ammonium sulphide and are reprecipitated together with those of As, Sb, Sn. All are dissolved in aqua regia, the excess of acid evaporated and NH_4Cl in concentrated solution added to separate $(NH_4)_2PtCl_6$, using alcohol for complete precipitation. To the filtrate, $FeSO_4$ solution is added to precipitate gold, which may be confirmed in a separate portion with $SnCl_2$. After removing the added iron, the sulphides of As, Sb, Sn, Mo are again precipitated, Sb and Sn removed with HCl and the As_2S_3 and MoS_3 dissolved in HNO_3. Arsenic is precipitated with Mg mixture, and Mo detected in the filtrate with Na_2HPO_4 or KSCN.

Yellow In_2S_3 and white GeS_2 also appear in Group II. In_2S_3 is not dissolved by $(NH_4)_2S_x$, but is converted into the white complex $(NH_4)_2[In_2S_4]$. If much acid is present in this group, indium passes on to Group III, where it appears with aluminium as $In(ONa)_3$, reprecipitated as $In(OH)_3$. It may be finally identified by the violet-blue flame colour, and by the microchemical test with rubidium chloride (379, 6).

Germanium sulphide is soluble in alkalis and in $(NH_4)_2S$. To confirm it, dissolve in conc. NH_4OH, evaporate to dryness in a Pt dish and add HF solution. Evaporate to dryness to remove S and Si, dissolve in dilute HF, filter and add K_2CO_3 solution to precipitate K_2GeF_6. This is gelatinous, and becomes crystalline on standing.

Group III. Hydroxides of La, Ce, Ti, Zr, Th, V, U come down in this group. The sodium peroxide treatment of the precipitate converts some into dioxides, as CeO_2, TiO_2, ZrO_2, ThO_2, which remain with Fe_2O_3 (and possibly MnO_2) and La_2O_3. This residue is dissolved in HCl and iron tested for in a portion as usual with $K_4Fe(CN)_6$. If present, H_3PO_4 solution is added to another portion to discharge the colour of $Fe^{\cdots}$, and then H_2O_2 is added. An orange-red colour destroyed by NaF solution indicates the presence of titanium.

To the remainder of the solution excess of saturated $(NH_4)_2C_2O_4$ solution is added, precipitating oxalates of La, Ce, Zr, Th. The first two are insoluble in excess of $(NH_4)_2C_2O_4$. From the filtrate, HCl reprecipitates $Th(C_2O_4)_2$, but not $Zr(C_2O_4)_2$. La and Ce

oxalates are boiled with 10 per cent. KOH solution to convert them into hydroxides, $La(OH)_3$ and $Ce(OH)_3$. This residue is filtered, dissolved in HCl, Ce identified in one half of the solution with H_2O_2, and La tested for in the other half with saturated K_2SO_4 solution, when the double sulphate, $La_2(SO_4)_3 3K_2SO_4$, crystallises out.

The solution obtained by warming the Group III precipitate with Na_2O_2 may contain Na_3VO_4 and Na_2UO_5, besides chromate, beryllate and aluminate. The beryllate is hydrolysed by boiling and $Be(OH)_2$ precipitated and filtered. The whole of this filtrate is acidified with acetic acid and mixed with lead acetate. V comes down as $Pb_3(VO_4)_3$ with $PbCrO_4$. This precipitate is dissolved in HNO_3, cooled well and shaken with H_2O_2 solution and ether in a separating funnel. A blue ethereal layer indicates Cr, while V gives a red to brown colour to the lower layer.

The filtrate from lead chromate and vanadate may contain Na_2UO_5 and $Al(ONa)_3$. Remove lead with H_2S, boil off excess and add concentrated $(NH_4)_2CO_3$ solution. $Al(OH)_3$ is precipitated; uranium remains in solution as $(NH_4)_4[UO_2(CO_3)_3]$. Concentrate, acidify with HCl and add $K_4Fe(CN)_6$, when the red uranium ferrocyanide will appear.

If phosphoric acid is present it should be removed by treatment of the filtrate from Group II with tin or $SnCl_2$ in presence of conc. HNO_3, before proceeding to Group III.

Group IV (the zinc group) may contain gallium sulphide, Ga_2S_3. This is soluble in very dilute HCl, and appears therefore with Zn and Mn. The flame test with this solution will reveal its presence, which may be confirmed by addition of $K_4Fe(CN)_6$, when the sparingly soluble pale bluish-white $Ga_4[Fe(CN)_6]_3$ is precipitated.

Group VI. Separation of rubidium and caesium from each other and from potassium is difficult and tedious. The spectroscope affords the best means of identification.

PART II

INTRODUCTION

396. In Qualitative Analysis the chemical nature of the constituents of a mixture or of a compound is investigated by converting those constituents into well-known and easily recognisable forms.

In Quantitative Analysis the same principles are involved, and the methods by which the quantitative determination of an element is carried out, are based upon the same reactions which serve for its qualitative recognition. The reactions selected, however, for quantitative work, must admit of the measurement of the amount of the constituent to be determined, either by converting it into a product which is of known composition, and can be weighed, or by measuring the volume of a prepared solution required to bring about the selected reaction.

The first is the **gravimetric** method, in which the substance to be determined is converted into another, of known composition, which is then accurately weighed. From this weight, the amount of the required constituent can be calculated.

The second is the **volumetric** method, in which solutions are employed, one containing the substance to be estimated, the other a known amount of a substance which has a definite reaction with the substance under examination. The volume of this second solution is measured, care being taken that the end of the reaction is sharply observed. This is usually attained by means of an **indicator**, such as litmus or methyl orange in acidimetry and alkalimetry.

Volumetric methods in general can be rapidly carried out, and require only simple apparatus. In many cases they admit also of great accuracy. On the other hand, gravimetric methods are often tedious and cumbersome, and at times require elaborate

apparatus. For rapidity of work, a volumetric method is to be preferred when one is available.

In all kinds of quantitative work, the most scrupulous care must be exercised to avoid possible errors; and if any slight error is even suspected, the experiment should be discarded and a new one commenced.

THE MEASUREMENT OF MASS

397. The balance. One of the operations most frequently carried out by the analyst is that of weighing. All quantitative

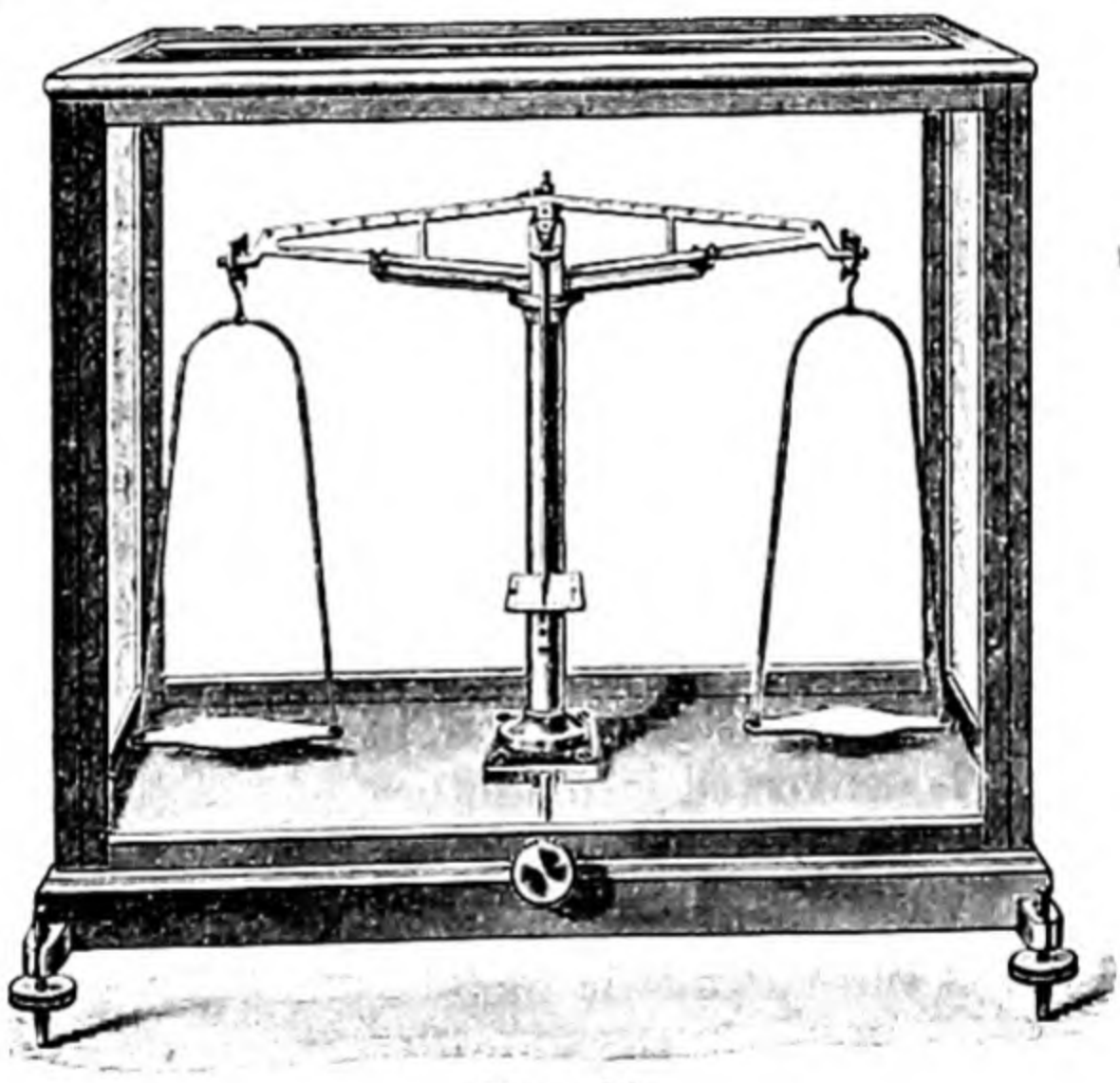


FIG. 64.

experiments, whether gravimetric or volumetric, depend in the first instance upon this operation, which is therefore of very great importance. It can be carried out with great precision, this depending on the form of balance used, in the manner about to be described.

Only the special features of the chemical balance, a general view of which is shown in Fig. 64, will be considered here. To eliminate friction as far as possible, the turning centres at the middle and ends of the beam consist of knife-edges of agate

bearing on plates of the same material. A method of suspension of the pan is shown in Fig. 65. When the balance is out of use, the knife-edges are not in contact with the plates, the beam being supported upon arms from the central pillar. By turning the lever in front of the balance, these supports are caused, by means of a small crank or cam, to be withdrawn from the beam, which then rests on its knife-edge and is thus placed in action. The beam must always be supported while the weights or other articles on the pans are being changed. The movement of the beam is indicated by a pointer which descends at a right angle from the middle of the beam to the scale near the foot of the pillar. When the balance is in proper adjustment the beam should come to rest in a horizontal position, and the end of the pointer is then opposite the middle of the scale, the pointer, the central knife-edge, and the middle line of the scale being all in the same vertical plane. The centre of gravity of the beam and its appendages is, of course, also in this plane, and should be below the fulcrum or central knife-edge, and as near to it as is practicable. Since the arms of the balance are precisely equal in length, and the pans with their supports should be of exactly equal weight, their interchange or removal, or the placing of equal loads in the pans, ought not to affect this equilibrium position of the beam and pointer. The coincidence, however, of the pointer with the scale centre is only realised if the balance is perfectly level, and any error in this respect must be rectified by means of the screws on the three supporting feet, before any other adjustment is made. An error in the zero may then be due to one or more of several causes :

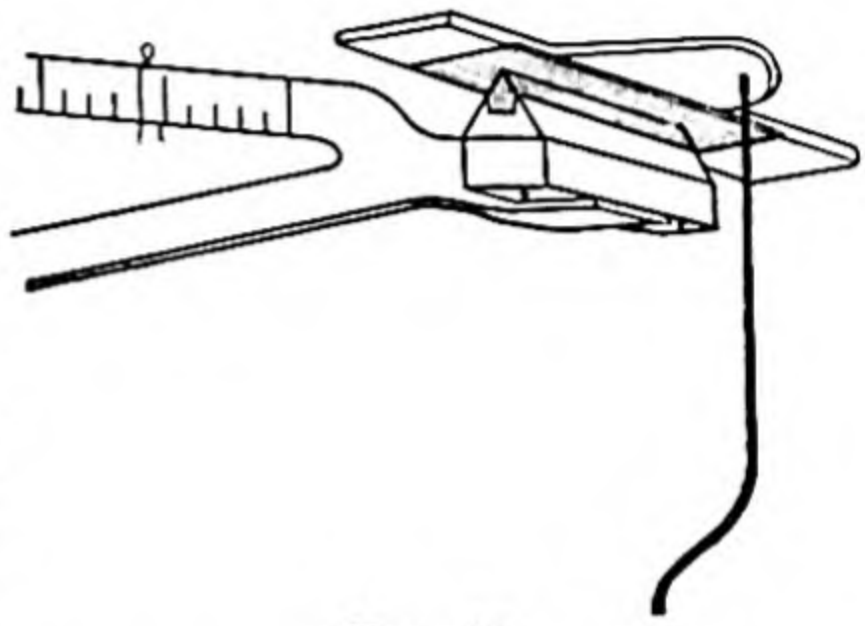


FIG. 65.

1. a mechanical defect in the placing of the pointer or scale or both ;
2. inequality in the lengths of the arms ;

3. a discrepancy in the weights of the two sides of the balance, arms or pans.

Further reference to these defects is made in the description of the methods of weighing, par. 399.

The zero may be adjusted, if desired, to coincide with the middle division of the scale by moving a small horizontal arm centred above the beam on the vertical axis, or a small nut moving horizontally above the beam from right to left. An exact coincidence, however, of the zero point with the centre of the scale is not absolutely necessary for correct weighing, since the zero is determined before each series of weighings, especially if the balance is used by more than one person.

The balance is enclosed in a glass case, the front of which, and usually also the back and sides, can be opened. The case must be kept closed to exclude dust, fumes, etc., and should contain a drying agent to keep the atmosphere dry. The case is supported on three metal feet, which can be raised or lowered with screws, so that the balance may be levelled. The table on which balances are supported should be as rigid as possible, preferably one built into an external wall.

Many details of the construction of the balance, which have not been described, will readily be understood by examining the one in use.

The sensibility of the balance, that is, the degree to which the beam is displaced by a very small difference between the weights in the two pans, depends on several conditions. These may be briefly explained from the diagram (Fig. 66).

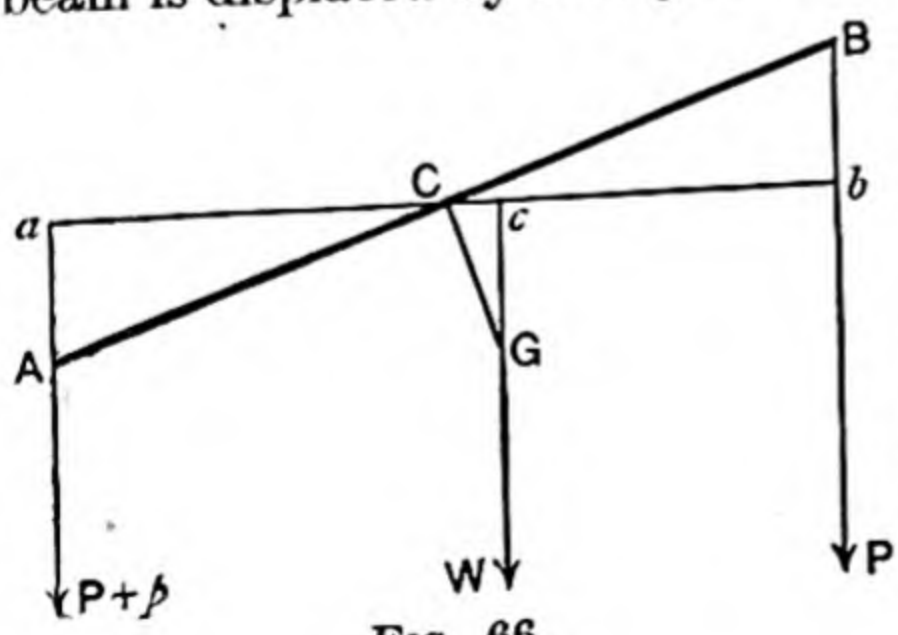


FIG. 66.

Let ACB represent the beam, the knife-edges being at those three points. Draw the horizontal line aCb, and the vertical lines aA, cG, Bb. G is the centre of gravity of the beam, including the pans and their loads. Let W be the total weight of beam, pans, etc., P and $P+p$ the loads on the pans

suspended from B and A respectively. And let the angle aCA, through which the beam is displaced by the small difference p in the loads, when equilibrium is reached, be called θ.

Then since the sum of the moments about C is zero, we have

$$(P+p)\times aC = P\times bC + W\times cC\ ;$$

but $$aC = bC\ ; \quad \therefore\ p\times aC = W\times cC.$$

Now the $$\angle cGC = \angle aCA = \theta\ ;$$

$$\therefore\ aC = AC\cos\theta \quad \text{and} \quad cC = CG\sin\theta\ ;$$

$$\therefore\ \frac{p}{W} = \frac{CG\sin\theta}{AC\cos\theta}; \quad \therefore\ \tan\theta = \frac{pAC}{WCG}.$$

Hence tan θ, and therefore also the angle θ through which the beam is turned, is independent of the load P in each of the pans; it is increased by increasing p, the excess load in one pan, by increasing the length of the beam, by diminishing W, the weight of the beam, and by diminishing the distance of the centre of gravity from the knife-edge. The last also increases the time of swing of the beam.

In practice these conditions are mutually antagonistic, and a compromise has to be effected. To ensure lightness, the beam is usually made with the central portion removed, which can be done without much loss of rigidity. The beam is also frequently made of aluminium or magnalium (an alloy of aluminium and magnesium), each having a low density. To lessen the time of swing of the beam, and therefore the time occupied in a weighing, the beam is shortened. This, of course, diminishes the sensibility, but the latter disadvantage is counterbalanced by making the depth of the centre of gravity below the knife-edge as small as is compatible with the stability of the balance.

This depth, and therefore also the sensibility of the balance, can be adjusted at will by raising or lowering a nut which turns, above the beam, on the central vertical axis.

In the foregoing discussion it is assumed that the three knife-edges are in one plane, which is the aim in all delicate balances. If this is not so, the sensibility will vary with the angle of displacement, that is, with the load, and will be increased if the ful-

crum lies below the plane containing the terminal knife-edges, and diminished in the contrary case. The latter is the more usual, especially as the beam tends to bend slightly with the load. The accompanying diagram (Fig. 67) serves to illustrate

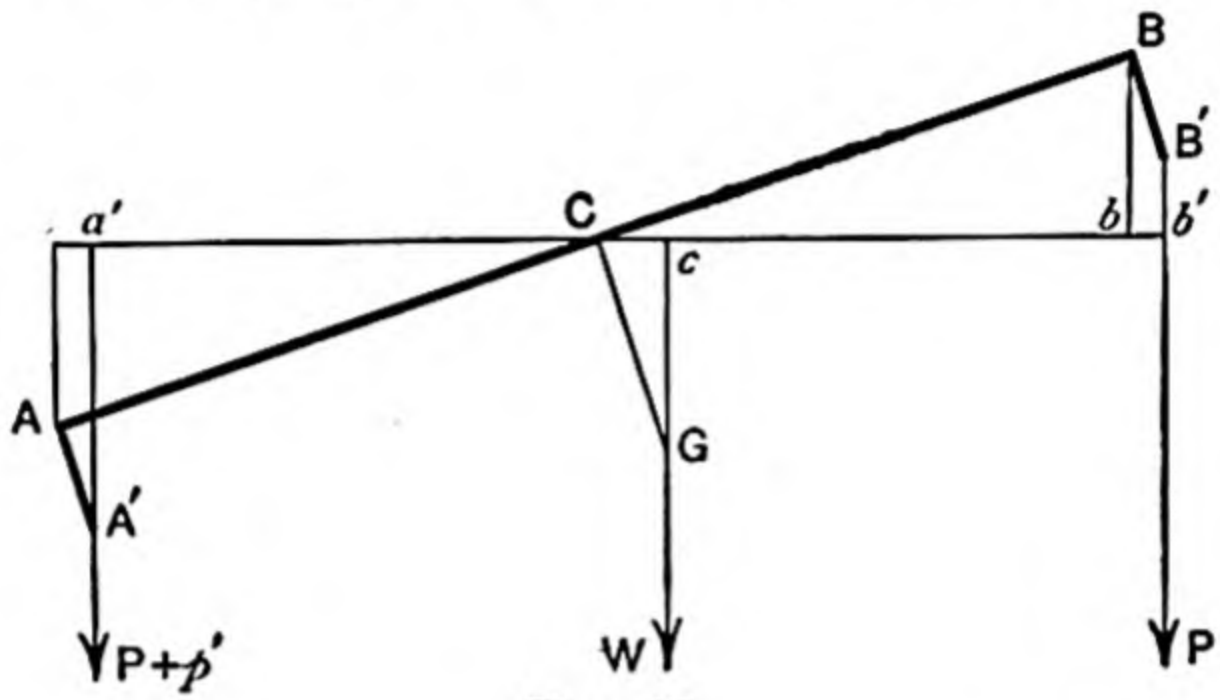


Fig. 67.

these relationships. The fulcrum is again at C, but the terminal knife-edges are now at A' and B' (compare Fig. 66), this being the condition under discussion. We now have

$$(P+p')a'C = P \times b'C + W \times cC\,;$$

since in this case now $a'C$ is $< Cb'$,

it is clear that the additional weight p' required to produce the same angular displacement θ, is greater than p (Fig. 66), when all three knife-edges are in one plane, and that the difference $(p'-p)$ increases with the displacement, that is, the sensibility diminishes with the load. Some makers arrange that in the unloaded balance the fulcrum is slightly below the plane containing the terminal knife-edges, and that the average load is just sufficient to bring the three into one plane.

398. The weights are arranged in a series from one gram up to 50 or 100 grams, or more, being usually made of brass and lacquered, gilded or platinised. An inspection of the box will show that any whole number can be made up within the limitations of the set. The fractional parts are arranged in corresponding values, and are made of platinum, gold, aluminium or other

metal. The weights must be very carefully handled, always moved by means of the forceps, and never touched with the fingers ; and they must be carefully protected against acid or other fumes, and dust. A slight tarnish, which usually appears after a time, has practically no effect on the weight, and this must on no account be rubbed off, or the weights will no longer be accurate.

It is customary in weighing to make up the value with the small weights to a centigram, and beyond this to use the rider, which is made of gold or platinum wire, and weighs one centigram. This is moved along the graduated beam until the exact counterpoise is attained. Thus the position of the rider on the beam completes the measurement to one tenth of a milligram. For still more accurate work milligram weights are used on the pan, and a milligram rider on the beam, by which means the weight is measured to one hundredth part of a milligram. For ordinary work, however, the centigram rider is quite sufficient. In some balances a bar fixed in front of, and parallel with the beam, is graduated for the whole length of the beam, beginning at one end instead of at the centre. A half centigram rider is then used, and the balance is in equilibrium when this is placed on the zero of the bar, that is, over the left-hand pan. A movement of the rider to the centre, which is marked 5, is thus equivalent to adding five milligrams, and the right-hand end records ten milligrams. The scale is thus more open, and greater accuracy is attainable.

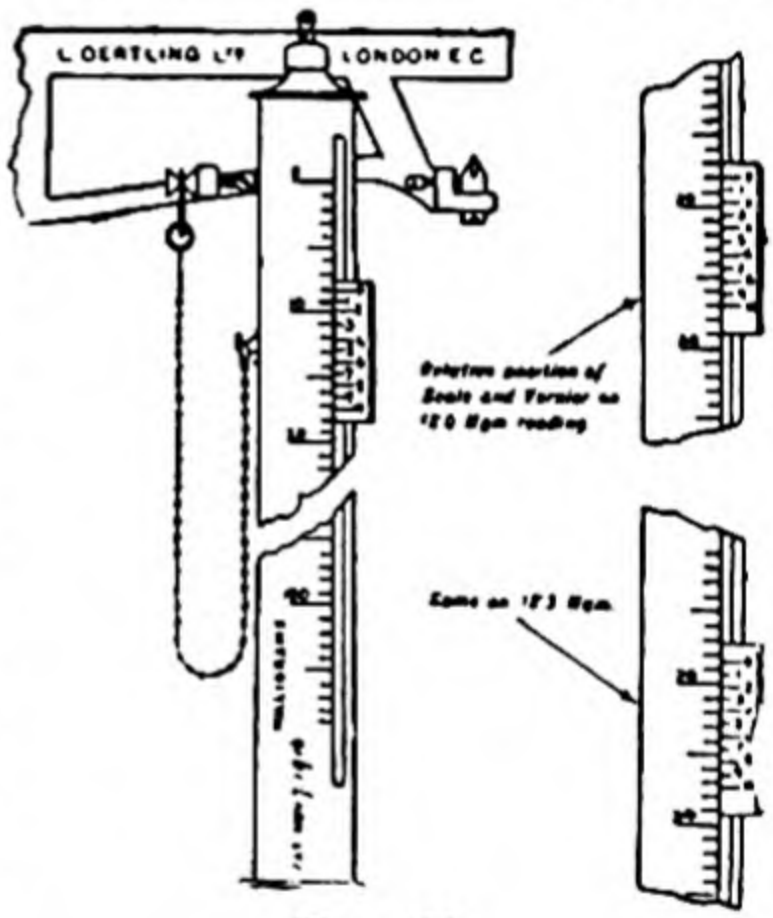


FIG. 68.

Many balances are now fitted with a chain arrangement by which the use of fractional weights can be eliminated and the operation of weighing accelerated. The chain is suspended at one end to the beam of the balance and at the other end either to a vernier which moves up and down a graduated vertical pillar and

is operated from outside the balance case or, with less accurate balances, to the rim of a graduated wheel, which shows the weight according to the length of chain wound on the wheel. Fig. 68 illustrates this so-called chainomatic arrangement.

To test the weights, the values of the several pieces should be carefully compared in terms of one of their number. The balance is first accurately adjusted so that the pointer is precisely at the zero of the scale. One of the gram weights is placed on the pan, and exactly counterpoised by placing brass clippings or fine wire on the other pan. When this has been done, the gram is replaced by another, and any deviation of the pointer noted. Since the value in milligrams of one scale division is known (399), the difference in weight between these two one gram pieces is thus determined. The third gram is examined in the same manner, the two gram piece with two one grams, the five with two and three ones, and so on. The fractions may be dealt with in a similar manner, and all together compared with the one gram.

The accuracy of the weights is usually greater than is required for ordinary quantitative work, but any errors should be known and allowed for when necessary.

399. The process of weighing. The student should be acquainted with the capabilities of the balance he is using, and should determine the sensibility with the pans empty, and then with loads of 25 and 50 grams in each pan. This may be done, and indeed the final approximation in all weighings should be made, by the **method of oscillations.** When the beam is released, the amplitude of vibration will be found to diminish very slowly, and a long time would elapse before the pointer finally came to rest, and so indicated the position of the zero. Instead of this, the position of the pointer on the scale is read at an odd number of turning-points, 3, 5, or 7, and the mean value found, those to the right being marked + and those to the left −. It is easy to read to one-half, or with a little practice to one-tenth, of a scale division. This mean value is the position of equilibrium, or the zero, for the unloaded balance. In an actual observa-

tion, the rider being at the middle of the beam, the readings were

$$-9{\cdot}3,\ 7{\cdot}5,\ 6{\cdot}1, \qquad \text{mean} = -7{\cdot}63,$$
$$+6{\cdot}2,\ 4{\cdot}8, \qquad \text{,,} \quad = +5{\cdot}5.$$

The zero point is thus $-1{\cdot}06$.

The rider was then moved to the first division to the right, making an addition of 1 mg., and the readings were then

$$-12{\cdot}0,\ 10{\cdot}4,\ 9{\cdot}1, \qquad \text{mean} = -10{\cdot}5,$$
$$+1{\cdot}1,\ -0{\cdot}4 \qquad \text{,,} \quad = +0{\cdot}35.$$

The zero is therefore $-5{\cdot}075$, that is, it has been moved $5{\cdot}075 - 1{\cdot}06$ or $4{\cdot}015$ divisions by the addition of 1 mg. The sensibility of the unloaded balance is therefore 4·015 divisions for 1 mg., or 1 scale division = 0·25 mg.

In a similar manner the sensibility for 1 mg. with 25 grams on each pan was found to be 4·105, and with 50 grams, 3·75, or the value of one scale division is 0·24 and 0·27 mg. respectively. In this case the sensibility diminishes slightly with a heavy load, as we should expect.

When the weight of a body has been found approximately, so that the pointer swings within the limits of the scale, the equilibrium point may then be found by the method of oscillations, and from the difference between this and the zero of the unloaded balance, the exact weight may be computed by adding the corresponding value in mg.

The method of **direct weighing** usually employed does not as a rule give the correct weight of an object. Any inequalities in the two sides of the balance will interfere with this; if, however, one always places the weights in the same pan, say that on the right, then the differences—and most working numbers are differences—are sufficiently correct for most purposes. The true weight, however, may be found by one of the following methods.

The method of **reversal** or interchange (*Gauss's* method) overcomes the error due to inequalities in the two sides of the balance. In this method the body is weighed first in one pan and then in the other. Let W be the true weight of the body, w_1 and w_2 the

observed weights in the two pans respectively, and a and b the lengths of the arms ; then

$$Wa = w_1 b, \quad \text{and} \quad Wb = w_2 a \ ;$$

$$\therefore \ W^2 ab = w_1 w_2 ab, \quad \text{or} \quad W = \sqrt{w_1 w_2}.$$

Thus the true weight is the geometrical mean of the two observed values ; if the latter are near each other, the arithmetical mean, $\frac{w_1 + w_2}{2}$, is sufficiently accurate.

The method of **substitution** or counterpoise (*de Borda's* method) also gives the true weight. In this method the body to be weighed is placed on one pan, with an approximate counterpoise on the other. Weights are then added to one side until an exact balance is secured. The body is now removed, and known weights added in its stead, until the balance is restored. The weights thus added give a measure of the true weight.

The **weight in vacuo** is required for very accurate work. On account of the buoyancy of the air, the effective weight of a body is less than the true weight, by the weight of the air displaced, and corrections must be applied in this sense both to the object and to the weights used to counterpoise it. When these are of approximately equal volume the correction is negligible ; but when the body to be weighed is bulky, as, for example, in weighing gases in large globes, it becomes imperative to reduce all weighings to vacuum.

400. Weighing bottles. When a substance is ready for analysis, it is placed at once in the weighing bottle. Some forms of this are shown in Fig. 69. The bottle should be of one diameter throughout, as a, b, and the ground glass stopper should not be cut, but blown from a glass tube, the flattened under side being retained. The two plain tubes shown at c, one fitting into the other, make a convenient form of weighing vessel for dried filters, etc. For insertion into a glass tube, a **boat** (Fig. 69, d) is often employed, as in the reduction of copper oxide or the ignition of antimony sulphide (**511**). These boats are made of porcelain, glass, or platinum.

In addition to these, watch-glasses, porcelain dishes and crucibles, etc., may be used for weighing a substance. On no

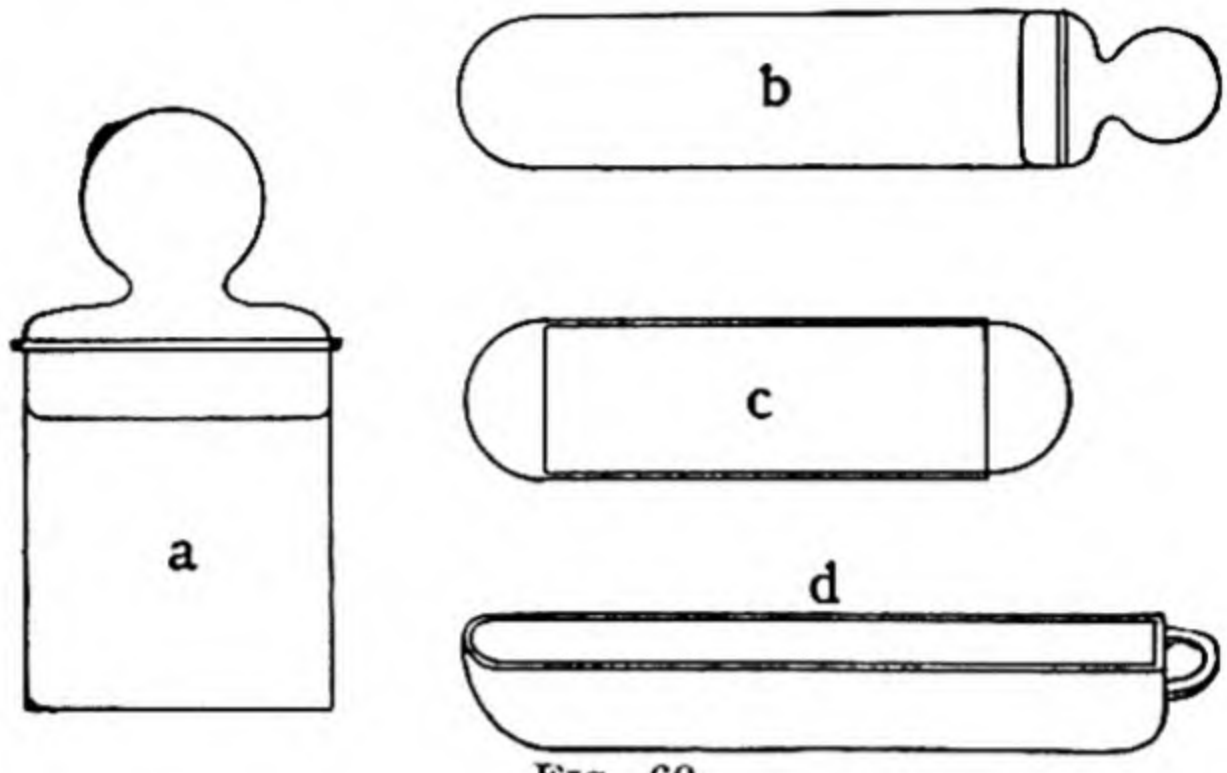


FIG. 69.

account should the substance to be weighed be placed directly on the pan.

Before weighing, a vessel must always be allowed to acquire, as nearly as possible, the temperature of the balance-room. With this object it is allowed to stand in the desiccator (20), in which also the weighing bottles should be kept.

THE MEASUREMENT OF VOLUME

401. Flasks. In volumetric analysis, vessels are required which have an accurately known volume. These are of various kinds. For adjusting the volume of a solution, the measuring flask (Fig. 70) is best. This is a flask with a long, narrow neck, fitted with a ground-in glass stopper. The flask contains the definite volume marked on the side, when filled to the mark etched round the neck. It is important to remember that these flasks *contain* the quantity indicated, and that when the liquid is poured out, a little always remains adhering to the sides of the vessel. The volume is ascertained by weighing with water at a known temperature, which is indicated on the flask. It is correct only at this temperature.

FIG. 70.

For an approximate measurement of the volume of a liquid, the measuring cylinder (Fig. 71) may be used.

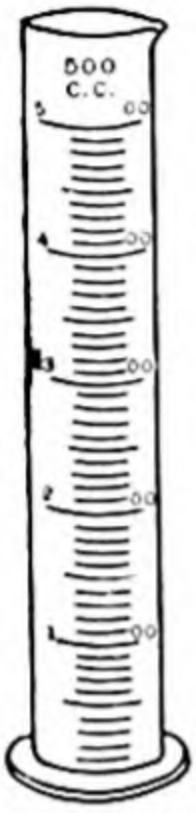


FIG. 71.

402. Burettes. A burette is a graduated glass tube, from which liquids may be run by means of a tap at the bottom, and the quantity run off is thus measured. The tap may be of glass, or made by a short piece of rubber tube closed by a clip, and terminating in a glass jet, as shown in Fig. 72, which represents the usual forms of Mohr's burette. For some liquids, as solution of potassium permanganate, the rubber tube should not be used. The burette is held in a stand, so that the volume of the liquid may not be affected by touching the tube with the hands. The diameter of the tube should be uniform, and as the graduations are often made by linear measurement, any lack of uniformity in this respect will introduce an error. Such error can be detected and corrected by calibration (404).

To read the burette it is important that the eye of the observer should be on the *same level* as the surface of the liquid, the position of which is to be read. Since the surface of the liquid is concave, it is essential to read always the position of the same portion of the surface. The bottom of the meniscus is the most clearly defined position, and as this is several millimetres behind the graduated wall of the burette, it is obvious that any change in the level of the eye will cause also a change in the reading. Many devices are employed to obviate this difficulty. The float is one of these (Fig. 72), and consists of a closed tube, fitting easily into the burette, with a circular mark etched on it, and loaded with a little mercury, so that it just floats in the liquid with the top projecting above the surface. The position of the etched circle on the float is then easily seen on the graduated tube.

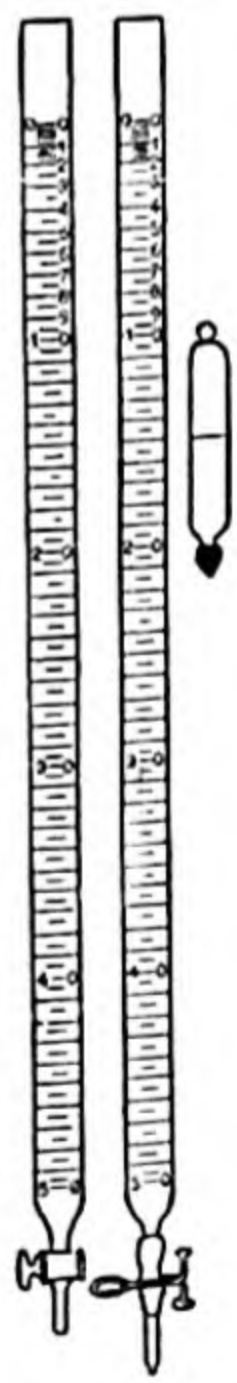


FIG. 72.

The burette is usually graduated in tenths of a cubic

centimetre. When the liquid is run from the burette, the sides of the tube remain wet with the liquid, and this slowly drains down. It will be found that on standing, the level of the liquid slowly rises by a small amount, and it is therefore necessary always to work at the same speed, and to read the burette after a constant interval of time.

403. Pipettes. The pipette is employed for removing measured quantities of liquids from other vessels, and consists of a long tube, with or without a bulb at the middle, and having a circular mark etched on the upper straight portion. The lower end is contracted to a narrow opening. This form of pipette, and also the straight graduated form, is shown in Fig. 73. The pipette *delivers* the volume of liquid it is graduated for, and when this has run from it, a little still remains in the lower end of the stem. As soon as the running has ceased, the end of the tube should be brought in contact with the liquid which has left it, and thus a little more is removed from the tube. The few drops which still remain are left in the tube, as they are taken into account in marking the pipette. By working always in the same manner, great uniformity in results can be attained.

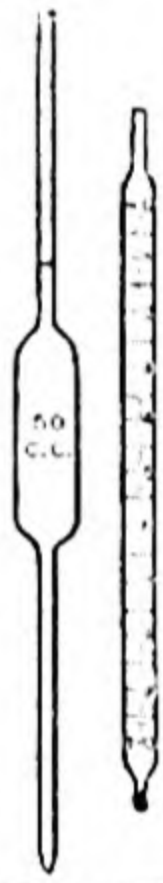


FIG. 73.

The pipette is graduated at the temperature marked upon it, and may not be accurate at other temperatures. The correctness or error of the pipette should always be determined by calibration.

404. Calibration of apparatus. By this term is meant the measurement of the error, if any, in the graduation of volumetric apparatus. One possible cause of such error in the case of the burette has already been mentioned. The method of calibration generally adopted is to fill the instrument to the mark with distilled water at a known temperature, or with mercury, and find the weight of this water or mercury. From the known density of water at the working temperature the exact volume can be calculated.

Measuring flasks are weighed empty, then filled with the water and weighed again. The pipette is calibrated by running the water into a weighing bottle, emptying the pipette in the manner which is to be adhered to afterwards, and then weighing the water. In the case of the burette, the water is run out into the weighing bottle 5 c.c. or 10 c.c. at a time, and each quantity carefully weighed. The error at each 5 or 10 c.c. can then be calculated, and it may be assumed to vary proportionally at the intermediate points. A curve may be drawn to obtain the errors at these points.

Cleansing volumetric apparatus. In the case of burettes and pipettes, fill with a saturated solution of potassium dichromate in conc. sulphuric acid, allow to stand for five minutes, run out, and rinse with water. With flasks and vessels of large capacity, pour in some of the solution, shake round to wet the sides, allow to stand, pour out and rinse.

A preliminary treatment with a strong solution of caustic potash, followed by rinsing, may be advisable in some cases. Solvents such as alcohol and ether may also be used.

Note. It has been recommended from the National Physical Laboratory that the litre and the millilitre (ml.), and not the cubic centimetre (c.c.), be used as units of volume, and most volumetric glassware is now marked in these units.

This followed the discovery of a slight error in the weight of the standard kilogram, originally defined as the weight of a cubic decimetre of water at 4° C. In 1901 the litre was defined as the volume occupied by a mass of one kilogram of pure water at its maximum density point and under standard atmospheric pressure.

As a result of extensive experiments,

$$1 \text{ litre} = 1000{\cdot}028 \text{ c.c.}$$

For practical purposes this small difference is negligible, but it cannot be ignored in experiments of high accuracy.

"1000 c.c." flasks which contain, at 15° C., a quantity of water having an apparent weight in air of 1000 g., actually have a capacity of 1002 c.c.

SECTION I

VOLUMETRIC ANALYSIS

ACIDIMETRY AND ALKALIMETRY

405. The foundations of volumetric analysis were laid by the researches of J. B. Richter (1762–1807), who showed that the proportions in which the various acids and bases neutralise one another are constant. The term "equivalent" had been used by Cavendish as early as 1767 for the weights of two acids neutralised by the same weight of a base. Richter's law of proportionality is an approximation to the law of reciprocal proportion. His discoveries helped greatly in establishing the laws of chemical action, and in the development of the Daltonian atomic theory. They led to the belief in the constant composition of salts, and on this belief is based the whole fabric of quantitative analysis.

The term "neutrality" now requires closer examination. When a solution is neutral, the concentration of hydrogen ions is the same as in pure water, namely :

$$[H^{\cdot}] = [OH'] = 0{\cdot}88 \times 10^{-7} \text{ at } 18°$$
$$= 1{\cdot}00 \times 10^{-7} \text{ at } 22°.$$

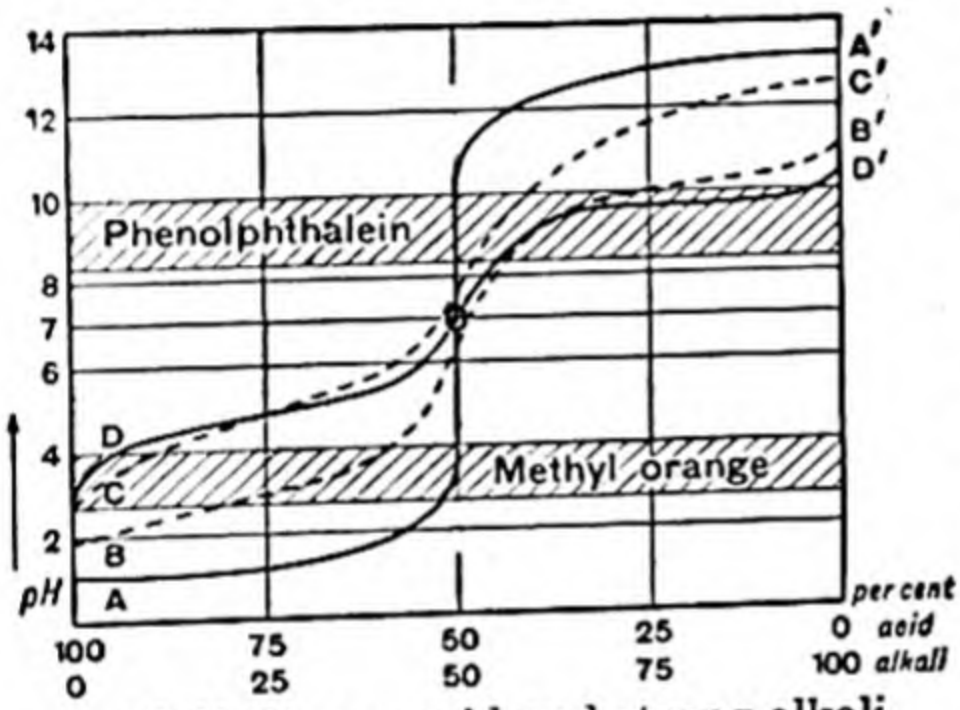
These concentrations are more conveniently expressed on the logarithmic scale, changing the sign, as suggested by Sörensen in 1909, so that the pH value (**86**), or hydrogen ion exponent, is

$$p\text{H} = -\log_{10} [H^{\cdot}] = 7.$$

This value holds for water and for solutions of salts formed by the union of strong acids with strong bases. But when either the acid or the base is weak, and the salt obtained on neutralisa-

tion is consequently hydrolysed to some extent, the equivalence point is not *p*H7, but has a value less or greater than 7 according as the alkali or the acid is relatively weak, and the solution of the pure salt therefore acid or alkaline as the case may be. The *p*H value of the equivalence point is given by a solution of the salt produced, at a concentration and temperature equal to those prevailing in the titration.

406. Electrometric methods are the most reliable for the determination of *p*H values.* Neutralisation curves may be constructed by plotting the *p*H values so obtained as ordinates, against the volume of acid or alkali as abscissae, in a given titration. Much useful information is obtained from a study of such curves, the general forms of which are illustrated in the diagram (Fig. 73A).



AOA' Strong acid and strong alkali
BOB' „ „ „ weak „
COC' Weak „ „ strong „
DOD' „ „ „ weak „

FIG. 73A.

In the first case, that of a strong acid neutralised by a strong base, the curve *AOA'* rises slowly, that is to say, the [H·] diminishes slowly, until the neutral point is approached, and the change in *p*H from about 4–10 is practically coincident with the equal volume ordinate, which it crosses at almost exactly *p*H7 This holds for 0·1 N. solutions; for N. solutions the vertical portion of the curve extends over a *p*H range of about 3–11, and in general, the more dilute the solutions, the less sharp is the end point. In the curve *DOD'*, for weak acid and weak alkali, the equivalence point is also very nearly *p*H7. Of the two dotted curves, *BOB'* crosses the middle ordinate below *p*H7, since the salt produced is hydrolysed and the solution slightly acid

* W. M. Clark, *The determination of hydrogen ions*, 3rd ed., p. 477 (1928). S. Glasstone, *Electrometric methods in chemistry*. Inst. Chem. lectures, 1934.

Similarly, for *COC'* the crossing takes place in the alkaline range above *p*H7.

Electrometric methods are, however, too elaborate and tedious for ordinary work, though they are of great value for coloured liquids.* In common practice the indicator method is more rapid, and sufficiently accurate for most purposes.

INDICATORS

407. The indicators used in acid-alkali titrations are generally weak organic acids or bases, which change colour at or near the equivalence point.

Wilhelm Ostwald † explained the colour changes on the ionic theory. He had shown that the uniform colour of a series of salts like the permanganates is due to the coloured anion common to the whole series, and is independent of the colourless cation. In all indicators, however, structural changes also occur in the formation of salts, as with phenolphthalein and methyl violet, and these are practically simultaneous with the ionic changes, which alone would not account for the colour. Hantzsch held that all indicators are either pseudo-acids or pseudo-bases, which undergo structural change during salt-formation.

Since different indicator acids have different dissociation constants, the neutral points of various indicators are found at varying values of the $H^{\cdot}$ concentration, as shown in the examples which follow. For any given reaction the most suitable indicator is the one whose colour change corresponds most closely with the *p*H of the equivalence point, and this depends, as explained above, on the degree of hydrolysis of the salt formed in the titration.

Phenolphthalein (294) is a very weak acid, very slightly ionised in solution. The unionised molecule is colourless, the anion pink ; thus (writing Ph for phthalein) :

$$\underset{\text{colourless}}{HPh} \rightleftharpoons H^{\cdot} + \underset{\text{pink}}{Ph'}$$

* S. Glasstone, *loc. cit.*, p. 8.

† *Foundations of analytical chemistry.*

and the dissociation constant of the indicator is

$$K = \frac{[H^{\cdot}][Ph']}{[HPh]}.$$

Thus, for a monobasic indicator acid, when half the indicator is transformed the hydrogen ion concentration is numerically equal to the dissociation constant of the indicator. The corresponding *p*H value, or $H^{\cdot}$ exponent, was called by Bjerrum the *indicator exponent*, p_1. It is a definite characteristic for any indicator.

The colour change of phenolphthalein represents a *p*H range from 8·3 (colourless) to 10 (deep red). It is therefore suitable for use in the titration of weak acids with strong alkalis, for the resulting salts, through hydrolysis, have a *p*H value greater than 7. On the other hand, it should not be used in the titration of weak bases such as ammonium hydroxide, whose salts with the weak indicator acid are largely hydrolysed, forming the colourless molecule :

$$NH^{\cdot}_4 + Ph' + H_2O \rightleftharpoons HPh + NH^{\cdot}_4 + OH'$$

excess of ammonia is required in order to produce the pink colour, and the end point is quite indefinite.

Methyl orange (263) is a strong acid, and at the same time a feeble base. The unionised alkali salt is yellow, the anion red ; and as the salts are partly ionised in solution, this has an orange colour. A trace of alkali causes association of the ions, and the solution becomes yellow. The *p*H range is from 2·9 to 4·0; the indicator may therefore be used in the titration of weak alkalis with strong acids, in which the equivalence point has a *p*H less than 7. Methyl red gives a more distinct colour change, with a *p*H range from 4·2 to 6·3, thus indicating a smaller acidity.

Most indicators have a transition range or sensitiveness covering 1·5–2·0 units of the *p*H scale. By selecting suitable indicators it is possible to include the whole experimental range of some 15 *p*H units. The following table illustrates this :

Indicator	*p*H range	Colour change
Tropoeolin OO - -	1·4 to 2·6	red to yellow
Bromophenol blue - -	2·8 ,, 4·6	yellow ,, blue
Methyl orange - -	2·9 ,, 4·0	red ,, yellow
Bromocresol green - -	3·6 ,, 5·2	yellow ,, blue
Methyl red - - -	4·2 ,, 6·3	red ,, yellow
Litmus - - - -	6·0 ,, 7·0	red ,, blue
Nitrazine yellow - -	6·4 ,, 6·8	yellow ,, blue
Neutral red - - -	6·8 ,, 8·0	red ,, orange
Phenol red - - -	6·8 ,, 8·4	yellow ,, red
Phenolphthalein - -	8·3 ,, 10·0	colourless ,, red
Tropoeolin O - - -	11·1 ,, 12·7	yellow ,, orange

Carbonates titrated with an acid leave a solution saturated with carbon dioxide, which alone causes an acidity equal to *p*H 3·5. Methyl orange is therefore suitable for use in the titration of carbonates. If boiled to expel the carbon dioxide, litmus or neutral red may be used as indicator.

Mixed indicators can be devised to increase the sensitiveness. Thus a mixture of two parts of phenolphthalein with one part of α-naphtholphthalein changes from pale rose through green to violet at *p*H 9·6. As this is the *p*H value for a solution of disodium phosphate, the mixture may be used in titrating phosphoric acid to the disodium salt.

Another example is a mixture of equal parts of neutral red and methylene blue, which gives a sharp change from violet-blue to green at *p*H7. It may be used to titrate acetic acid with ammonia or *vice versa*. These have approximately equal dissociation constants, and the end of the reaction comes when *p*H = 7. But in general the titration of weak acids with weak alkalis is to be avoided ; the curve *DOD′* in Fig. 73A shows that a change of 1·5–2·0 units in *p*H value, which corresponds with the colour change of most indicators, requires the addition of 2–3 c.c. of 0·1 N. acid or alkali ; in fact, no single indicator gives a sharp end point. Strong acid and strong alkali, on the other hand (curve *AOA′*), may be titrated with the aid of any indicator changing within the *p*H range 4–10.

Thymol blue (6 parts) with cresol red (1 part) changes from violet to rose over a *p*H range from 8·4 to 8·2, corresponding to the *p*H of sodium bicarbonate. Phenolphthalein is used in 421 because it becomes colourless at approximately this value, but it has the disadvantage of being a one-colour indicator.

Screened indicators contain, in addition to the indicator, a coloured substance which undergoes no change over the *p*H of the indicator, but makes the colour change of the latter more distinct without affecting its transition range. They were introduced by Luther in 1907, when he added indigo in the use of methyl orange. Indigo must be carefully tested for acidity. Xylene cyanole FF (1·4 g.) with methyl orange (1 g.) in 500 c.c. of 50 per cent. alcohol changes from green to magenta with a neutral grey colour at *p*H 3·8.

The **universal indicator** is a mixture of indicators which changes through the complete range of spectrum colours from red to violet in the correct order as the *p*H changes from 3 to 11. Thus the *p*H of a solution can be found readily by comparing the indicator colour with standard colour solutions.

A list of the colours with the corresponding acidities is always supplied with the indicator

In using indicators it should be remembered that the *p*H of a solution is influenced by the temperature, chiefly owing to the increase in the dissociation constant of water, and by dilution, both of which affect hydrolysis; and also by the presence of foreign salts. An indicator which is good under one set of conditions may thus be unsuitable for the same titration at a different concentration or temperature. The salt effect is slight, usually positive for acidic indicators and negative for basic ones, and diminishes with rising temperature.

BUFFERING

408. Buffer solutions The colour standards referred to above must be prepared in such a way that the *p*H does not change. For this and other purposes *p*H values are stabilised in the following manner.

Acetic acid is only slightly ionised, and this feeble ionisation is diminished, in accordance with the mass law, by the addition of one of its soluble salts, as sodium acetate :

$$\frac{[H^{\cdot}]\,[CH_3COO']}{[CH_3COOH]} = K.$$

If now a little hydrochloric acid is added, the additional $H^{\cdot}$ ions unite with acetate ions to form unionised acetic acid, and the increase in $[H^{\cdot}]$ is very slight. Similarly an addition of sodium hydroxide unites with the acetic acid, and again there is very little decrease of the $[H^{\cdot}]$. Such a solution is said to be " buffered " against change of hydrogen ion concentration. Alkaline buffer solutions may be prepared with mixtures of ammonium hydroxide or other weak alkali and one of its salts.

Buffer action is greatest within a narrow range indicated on the titration curve, and varies with the ionisation of the acid or alkali used, the concentrations of these, and the proportion of the salts employed. By suitable adjustment of these factors a series of buffer solutions or regulators can be prepared, with *p*H values that are easily reproduced. The exact values are determined electrometrically.

The colour standards supplied with the universal indicator are prepared with buffer mixtures. Comparison flasks used to show the indicator colour at the equivalence point should also be buffered ; they are then unaffected by atmospheric carbon dioxide or by the glass. Electrometric measurements of *p*H can be made accurately only in suitably buffered solutions.

Many common reactions are partly dependent on buffering, and were in use long before this matter was investigated by Fernbach and Hubert in 1900. In the precipitation of basic ferric acetate, for example, the excess of alkali acetate (**203, 3 ; 531**) ensures a fairly constant *p*H value during the process. A similar effect is due to the excess of acetate in the phosphoric acid separation (**360**) and in the precipitation of the 8-hydroxyquinoline salt of aluminium (**500 B**), of lead chromate (**506 B**) and of lead molybdate (**517 B**). Alkaline buffer mixtures are used in the NH_4OH—NH_4Cl precipitation of the iron group (**356**). and in that of Zn, Mg and Mn as phosphates (**508 A, 516 B**).

STANDARD ACIDS AND ALKALIS

A normal solution is one which contains the equivalent weight in grams of the principal reacting ion dissolved in one litre of the solution. A slight modification of this definition is necessary when solutions of oxidising agents are considered (see par. 429).

409. N. sodium carbonate. As this substance can be obtained in a very pure state, it forms a useful standard alkali, against which acids may be checked whose concentrations in the pure state are not accurately known.

Heat in a weighed platinum dish about 45 g. of pure anhydrous sodium bicarbonate, with constant stirring, and without fusing, until after cooling in the desiccator the weight is constant.

Remove some of the pure carbonate till exactly 26·5 g. remain. Add hot water and heat till dissolved. Cool, transfer to a 500 c.c. flask, make up to the mark and mix well by pouring to and from a dry beaker. The solution contains 0·053 g. of sodium carbonate in 1 c.c. and is therefore normal.

Sodium oxalate, $Na_2C_2O_4$, is very pure: the required amount may be heated as above until the resulting pure carbonate is of constant weight.

410. N. sulphuric acid. Measure 28 c.c. of the concentrated acid, which contains about 98 per cent. H_2SO_4, into water and cool. Transfer to a litre flask, make up to the mark and mix well. The solution will be roughly normal.

Rinse a clean burette twice with a little of the acid, and fill it. The level of the acid need not be exactly at the zero.

Similarly rinse a 25 c.c. pipette with the N. sodium carbonate and fill it. Allow the alkali to flow into a 250 c.c. conical flask, then touch the surface of the liquid with the end of the pipette, but do not blow out the remaining liquid (see 403).

Add to the alkali one or two drops of litmus solution, read the position of the acid in the burette, enter this at once in the note-book, and run the acid carefully into the flask till the litmus just turns red. Boil off the carbon dioxide: the litmus again turns blue. Add more acid until, after boiling, one drop turns the litmus red. Again read the burette. NOTE.—Before the end of

every titration the liquid on the sides of the flask should be washed down.

Methyl orange also may be used, without boiling (407). Lunge* pointed out that the indicator used in standardising the acid or alkali must be used also in later practice with these solutions.

Repeat the titration, using litmus or methyl orange, till three concordant results are obtained. Average these, and calculate the strength of the acid as follows :

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2.$$

then 1 c.c. of N. Na_2CO_3 solution contains 0·053 g. Na_2CO_3 ;

$\therefore$ 1 ,, ,, ,, will neutralise 0·049 g. of H_2SO_4.

Now suppose 24·2 c.c. of acid have been required for 25 c.c. of the N. sodium carbonate. These must contain

$$25 \times 0{\cdot}049 \text{ g. of } H_2SO_4.$$

$\therefore$ 1 c.c. of the sulphuric acid contains

$$\frac{25 \times 0{\cdot}049}{24{\cdot}2} = 0{\cdot}0506 \text{ g. } H_2SO_4.$$

Another method of calculation is the following :

25 c.c. of N. Na_2CO_3 solution neutralise 24·2 c.c. of H_2SO_4 ;

$$\therefore \text{ the } H_2SO_4 \text{ solution is } \frac{25}{24{\cdot}2} \text{ of normal ;}$$

$$\therefore \text{ 1 c.c. of the acid contains } \frac{25}{24{\cdot}2} \times 0{\cdot}049 = 0{\cdot}0506 \text{ g. } H_2SO_4.$$

If it be desired to make the sulphuric acid normal, 25 – 24·2 or 0·8 c.c. of water must be added to each 24·2 c.c. of the sulphuric acid. Measure the acid left, in a measuring cylinder, add the calculated quantity of water and again titrate. The solutions should be equivolumetric, i.e. the sulphuric acid is normal. If not, again add a calculated quantity of water.

Instead of making the acid exactly normal, it can be used as $\frac{25}{24{\cdot}2}$ N. = 1·033 N.

* G. Lunge, *Z. angew. Chem.*, **18**, 1520 (1905).

A rapid and accurate method for preparing standard solutions of sulphuric acid is that devised by Marshall.* Some very pure sulphuric acid is diluted with half its volume of water, and when cold, the specific gravity is determined carefully at 18°, or 15°, or 15·5°. To ensure accuracy within 0·1 per cent. in the standard solution, this determination of specific gravity must be correct to 0·0005, and the temperature must be known to 0·5°. If a Sprengel tube of 25 c.c. capacity be employed, the weighings must be correct to 0·01 gram. The minimum error in the standard solution caused by errors in those measurements, occurs when the diluted acid contains 80 per cent. of sulphuric acid, and is 0·11 per cent. for an error of 0·001 in specific gravity, or of 0·1° in temperature. The concentration of this acid is now calculated by means of formulae based upon the work of Pickering † on the sp. gr. of sulphuric acid solutions :

$$P = 86 \times S_{15} - 69{\cdot}00,$$

$$P = 86 \times S_{15{\cdot}5} - 68{\cdot}97,$$

$$P = 86 \times S_{18} - 68{\cdot}82,$$

where P is the percentage of H_2SO_4, and S the specific gravity. The percentages so calculated do not deviate more than 0·04 from the truth, if they lie between 66 and 81. The following general formula may be used between 0° and 40°, for acids containing 62–82 per cent. H_2SO_4 :

$$P = S(85{\cdot}87 + 0{\cdot}05T - 0{\cdot}0004t^2) - 69{\cdot}82,$$

where S is the specific gravity at $T°$ compared with that of water at $t°$.

Having found the concentration of this acid, the standard solution may at once be made by diluting to the required extent. If A be the number of grams H_2SO_4 per litre of the standard solution, n the number of litres to be prepared, and W the weight of acid required, then

$$W = nA \times \frac{100}{P}.$$

* A. Marshall, *J. Soc. Chem. Ind.* 1899, **4**, 1091.

† S. U. Pickering, *J.C.S.* 1890, 64.

The acid prepared in this manner should be compared with that standardised against sodium carbonate (409).

411. **N. sodium hydroxide.** Sodium hydroxide powder (98 per cent). may be used. Roughly weigh out enough to make a litre of solution slightly stronger than normal, say 45 g. Dissolve in water, and when cold, make up to a litre.

Take 25 c.c. in a pipette, place in a titrating flask, add one drop of neutral red or nitrazine yellow solution and run in the sulphuric acid (now normal) as before. Assume 25·3 c.c. of acid are required. Then the alakali is $\frac{25{\cdot}3}{25}$ normal, i.e. 1 c.c. contains

$$\frac{25{\cdot}3}{25} \times 0{\cdot}040 = 0{\cdot}041 \text{ g. of NaOH.}$$

If the solution is required to be normal, add 0·3 c.c. of water for each 25 c.c. of alkali, and check the value again.

412. **N. oxalic acid.** Crystallised oxalic acid, $(COOH)_2 2H_2O$, may be obtained in a very pure state, but precautions must be taken against loss of water. Since the acid is dibasic the equivalent weight is half the molecular weight ; and a litre of normal oxalic acid contains 63 grams of the crystals. This solution offers a convenient means of standardising solutions of alkali hydroxides, which are of uncertain composition.

413. **N. hydrochloric acid, from N. oxalic or other acid and an alkali of unknown concentration.**

Prepare an approximately normal solution of hydrochloric acid by diluting 20–25 c.c. of the concentrated acid to 250 c.c.

Dissolve 8–10 g. of sodium hydroxide, weighed roughly and quickly, in cold distilled water ; cool and dilute the solution to about 250 c.c. The exact concentration of this solution is not known, but it is such that when titrated against the acid there is not too great a discrepancy between the volumes used.

Fill a burette with the alkali, and titrate 20 c.c. of the hydrochloric acid, using methyl orange as indicator. Make three concordant titrations and take the average ; let this be x c.c.

Repeat the titration against 20 c.c. of the normal (or any other standard) acid available, following the same method. Let the titration now be y c.c.

Then the normality of the hydrochloric acid is $\frac{y}{x}$ of that of the standard, or generally, and for all similar estimations, the concentration of the unknown acid is $\frac{y}{x}$ of that of the standard.

DETERMINATION OF EQUIVALENTS OF METALS

414. The equivalent weight of a metal, its oxide or its carbonate is that weight which neutralises one litre of normal acid. The equivalent of the metal can be obtained by subtracting 8 from the equivalent of its oxide, or 30 from the equivalent of its carbonate.

Magnesium. Weigh accurately about 0·4 g. of the metal into a titrating flask, and add 50 c.c. of normal sulphuric acid. The metal dissolves completely. Titrate the excess of acid with 0·1 N. alkali, using neutral red as indicator, and thus find the volume of acid neutralised by the magnesium. Calculate the weight of magnesium required to neutralise one litre of the normal acid.

In the same way find the equivalents of zinc and aluminium. It will be better to use a more concentrated acid, and for aluminium, hydrochloric acid is a better solvent.

Zinc. Use as before 50 c.c. of the normal acid. Weigh out and dissolve in the acid about 1·5 g. of zinc oxide. Titrate the excess of acid and calculate the weight of oxide required to neutralise one litre of the acid. Subtract 8 from your result to obtain the equivalent of the metal.

Repeat the experiment using other oxides.

Calcium. In this case it is preferable to use normal hydrochloric acid. Take 50 c.c. of the normal acid. Weigh out carefully about 2 g. of finely ground Iceland spar and add it to the acid. When all action has ceased, titrate the excess of acid, using methyl orange as indicator. Calculate the equivalent of the carbonate, and subtract 30 to obtain that of the metal.

Carbonates of other metals also may be used, but care must be taken that the substance is the pure normal carbonate.

From such experiments the molecular weights of the compounds used may be deduced, if the valency of the metal in that compound is known.

415. Estimation of KOH in caustic potash. Use 0·5N. H_2SO_4. Weigh a dry corked test-tube containing about 10 g. of the caustic potash. Transfer the caustic potash to water in a 250 c.c. flask, and reweigh the tube and cork. Allow the caustic potash to dissolve, and, when cold, make up to 250 c.c. and mix well. Use 25 c.c. for each titration, with litmus, neutral red, or methyl orange as indicator. Enter the results as under.

Tube and caustic potash -	21·07 g.
Tube - - - -	12·95 g.
Caustic potash - -	8·12 g.

TITRATIONS :

1	2	3	
24·98	26·88	25·52	
0·52	2·39	1·10	Average 24·46 c.c.
24·46	24·49	24·42	

CALCULATION :

$$2KOH + H_2SO_4 = K_2SO_4 + H_2O.$$
$$2 \times 56 \qquad 98$$

1 c.c. of 0·5N. H_2SO_4 will neutralise $0·5 \times 0·056$ g. KOH.

∴ 24·46 c.c. of 0·5N. H_2SO_4 will neutralise $0·5 \times 0·056 \times 24·46$ g. KOH ;

but 24·46 c.c. of 0·5N. H_2SO_4 neutralise 25 c.c. of potash solution.

∴ 25 c.c. of the potash solution contains $0·5 \times 0·056 \times 24·46$ g. KOH.

∴ 250 c.c. of the potash solution or 8·12 g. of the solid contain $0·5 \times 0·056 \times 24·46 \times 10$ g. KOH.

$\therefore$ The weight of KOH in the solid

$$= \frac{0{\cdot}5 \times 0{\cdot}056 \times 24{\cdot}46 \times 10 \times 100}{8{\cdot}12} \text{ per cent.}$$

$$= \underline{83{\cdot}1} \text{ per cent.,}$$

or, the caustic potash solution is $\frac{24{\cdot}46}{25}$ of 0·5N.

$\therefore$ 250 c.c. of the solution or 8·12 g. of the solid contain

$$\frac{24{\cdot}46}{25} \times \frac{56}{2} \times \frac{1}{4} \text{ g. KOH.}$$

$\therefore$ The weight of KOH in the solid

$$= \frac{24{\cdot}46}{25} \times \frac{56}{2} \times \frac{1}{4} \times \frac{100}{8{\cdot}12} \text{ per cent.}$$

$$= \underline{83{\cdot}1} \text{ per cent.}$$

416. Estimation of Na_2CO_3 in soda crystals. Powder the crystals and, if moist, dry between layers of filter paper. Weigh out about 15 g. from a stoppered weighing bottle, dissolve in water in a 250 c.c. flask, and make up to the mark. Titrate 25 c.c. at a time, using methyl orange as indicator.

Bottle and crystals - -	24·39 g.
Bottle - - - -	10·20 g.
Crystals - - -	14·19 g.

TITRATIONS:

1	2	3	
21·29	21·14	21·02	
2·18	2·04	1·90	Average 19·11 c.c.
19·11	19·10	19·12	

$$\underset{106}{Na_2CO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + H_2O + CO_2.$$

Suppose the acid to be 0·52 normal.

1 c.c. of 0·52N. H_2SO_4 will neutralise 0·52 × 0·053 g. Na_2CO_3.

$\therefore$ 19·11 c.c. of 0·52N. H_2SO_4 will neutralise 0·52 × 0·053 × 19·11 g. Na_2CO_3,

but 19·11 c.c. of 0·52N. H_2SO_4 will neutralise 25 c.c. of the soda solution.

∴ 25 c.c. of the soda solution contain $0·52 \times 0·053 \times 19·11$ g. Na_2CO_3.

∴ 250 c.c. of the soda solution or 14·19 g. of the crystals contain $0·52 \times 0·053 \times 19·11 \times 10$ g. Na_2CO_3.

∴ The percentage of Na_2CO_3 in the crystals

$$= \frac{0·52 \times 0·053 \times 19·11 \times 10 \times 100}{14·19}$$

$$= \underline{37·1},$$

or, the soda solution is $\frac{19·11}{25}$ of 0·52N.

∴ 250 c.c. of the solution or 14·19 g. of the crystals contain

$$\frac{19·11}{25} \times 0·52 \times \frac{53}{4} \text{ g. } Na_2CO_3.$$

∴ The percentage of Na_2CO_3 in the crystals

$$= \frac{19·11}{25} \times 0·52 \times \frac{53}{4} \times \frac{100}{14·19}$$

$$= \underline{37·1}.$$

417. Estimation of HCl in concentrated hydrochloric acid. (*a*) Given 0·52N. NaOH. Pour 8 to 10 c.c. of the concentrated acid into a weighed stoppered bottle. Weigh the bottle and acid. Wash the contents into a 250 c.c. flask and make up to the mark. Take 25 c.c. for each titration, and run in the sodium hydroxide solution, using neutral red as indicator. Enter the data and calculate the result as shown in the preceding example. Many prefer to take 25 c.c. of the alkali and run the acid from the burette.

(*b*) Given 0·52N. H_2SO_4. Make roughly a solution of an alkali (NaOH) about half normal. Find the amount of the sulphuric acid and of the diluted hydrochloric acid required to neutralise 25 c.c. of the alkali solution. Let these be respectively 18 c.c. and 15 c.c. Then the diluted hydrochloric acid is $\frac{18}{15} \times 0·52$N. ;

therefore the weight of acid in the 250 c.c., i.e. in the weight of the concentrated acid used, can be found.

Test your result by finding the sp. gr. of the concentrated acid and referring to tables (568).

418. Estimation of acetic acid. Sodium acetate gives an alkaline solution of *p*H 8·0. The indicator used should show this end point. Phenolphthalein can be used. Weigh out about 4 c.c. of glacial acetic acid and carry out the estimation by either method (*a*) or (*b*) above.

419. Estimation of boric acid and borax. Boric acid has a *p*H only slightly greater than that at which methyl orange changes colour. This indicator can therefore be used to estimate borax by titration with hydrochloric acid solution. Sulphuric acid does not give a sharp end point.

Weigh accurately 3 to 4 g. of borax, dissolve in hot distilled water and, when cold, make up to 250 c.c. Titrate 25 c.c. at a time with 0·1N. HCl and retain the neutral liquid for the next method. Calculate the amount of borax :

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

The boric acid is now free. When an equivalent amount of sodium hydroxide is added, the salt produced is alkaline owing to hydrolysis. In the presence of glycerol or mannitol, this hydrolysis is considerably decreased, so that on the completion of the reaction :

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O,$$

the *p*H is such that phenolphthalein can be used as indicator. The glycerol must, of course, be neutral. It should be tested for acidity, and a correction made if necessary.

Use the boric acid solution produced in the first part of the experiment, add 15 c.c. of glycerol for each titration, and titrate with 0·1N. NaOH.

420. Estimation of NH_3 in liquor ammoniae. Place 150 c.c. of N. H_2SO_4 in a 250 c.c. flask. From a burette add 5 c.c. of con-

centrated aqueous ammonia, close the flask and shake. Make up to the mark with water, mix well and titrate the excess of acid with 0·1N. alkali. Alternatively the concentrated ammonia may be weighed by placing about 5 c.c. in a weighed, stoppered weighing bottle and weighing again. Then dilute with water to minimise loss, transfer to the acid and proceed as above. The NH_3 is calculated as a percentage on either the volume or the weight of the original liquor.

421. Estimation of alkalis in soda ash. Soda ash consists mainly of sodium carbonate, but may contain also small quantities of bicarbonate or of hydroxide.

When sufficient standard sulphuric acid is added to a solution of pure sodium carbonate to convert it to the bicarbonate, the *p*H of the solution is about 8·3. Phenolphthalein will indicate this point. The mixed indicator (407) is more accurate. Further addition of acid will convert the bicarbonate to sulphate, and for this stage methyl orange is the most suitable indicator.

$$2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4,$$
$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2.$$

It is clear that the quantities of acid used in the two stages are equal. If, however, sodium hydroxide be present, the quantity of sulphuric acid used in the first stage will be greater than that used in the second by an amount corresponding to this sodium hydroxide. On the other hand, if sodium bicarbonate be present, the quantity used in the second stage will be greater than that used in the first by an amount corresponding to the bicarbonate.

Weigh out about 10 g. of soda ash, dissolve in warm water, cool and make up to 250 c.c. Take 25 c.c., add phenolphthalein as indicator, and run in standard sulphuric acid solution till the pink colour is destroyed. Take the reading. Add a drop of methyl orange, and run in more acid till the colour changes. Repeat and obtain three concordant results.

422. Estimation of NaOH and Na_2CO_3 in a mixture of the two substances. Weigh out a suitable quantity of the mixture, dis-

solve in water and make up to 250 c.c. Titrate 25 c.c. with standard acid, using methyl orange as indicator. This will give the total alkali.

To another 25 c.c. add barium chloride in excess to render the carbonate insoluble. Titrate with standard hydrochloric acid, using phenolphthalein as indicator. The indicator will become colourless when all the hydroxide is neutralised and before any of the carbonate has been dissolved.

423. Estimation of Na_2CO_3 and K_2CO_3 in a mixture of the two substances. Use 0·5N. H_2SO_4. Weigh out accurately about 7 g. of the mixture, dissolve in hot water, cool and make up to 250 c.c. Titrate 25 c.c. at a time, using methyl orange as indicator.

1 c.c. 0·5N. H_2SO_4 will neutralise 0·0265 g. Na_2CO_3,
1 c.c. ,, ,, ,, 0·0345 g. K_2CO_3.

CALCULATION. Let the weight of the mixture taken be 6·82 g., and the volume of acid used for each titration be 21·68 c.c. Then the volume required for 250 c.c. or 6·82 g. of the mixture will be 216·8 c.c.

First method. Let x = weight of Na_2CO_3,

then $6{\cdot}82 - x =$,, ,, K_2CO_3;

then $$\frac{x}{0{\cdot}0265} + \frac{6{\cdot}82 - x}{0{\cdot}0345} = 216{\cdot}8,$$

from which $x = 2{\cdot}18$;

$$\therefore \text{ the percentage of } Na_2CO_3 = \frac{2{\cdot}18}{6{\cdot}82} \times 100 = \underline{31{\cdot}8}.$$

Second method. If the substance were all pure sodium carbonate the volume of acid required would be

$$6{\cdot}82 \div 0{\cdot}0265 = 257{\cdot}7 \text{ c.c.},$$

and if all potassium carbonate,

$$6{\cdot}82 \div 0{\cdot}0345 = 197{\cdot}7 \text{ c.c.}$$

$$\therefore \frac{\text{wt. of } Na_2CO_3}{\text{wt. of } K_2CO_3} = \frac{216{\cdot}8 - 197{\cdot}7}{257{\cdot}7 - 216{\cdot}8} = \frac{19{\cdot}1}{40{\cdot}9}.$$

$$\therefore \text{ the percentage of } Na_2CO_3 = \frac{19{\cdot}1}{40{\cdot}9 + 19{\cdot}1} = \underline{31{\cdot}8}.$$

Similar experiments can be carried out with mixtures of other carbonates, oxides, etc.

As additional experiments, the concentrations of solutions of nitric acid, ammonia, oxalic and tartaric acids, can be estimated, care being taken to use suitable indicators.

Alkaline earth hydroxides may be titrated with standard hydrochloric acid, until phenolphthalein is colourless.

If carbonate also is to be estimated, as in lime, the total alkali ($CaO + CaCO_3$) is determined by dissolving a weighed sample in a measured excess of N. HCl and titrating the excess of acid. The $CaCO_3$ is then found by difference.

Soluble salts of metals that give insoluble carbonates (or hydroxides) may be estimated by precipitating the carbonate (or hydroxide) from a weighed sample with a measured excess of N. Na_2CO_3 (or NaOH). After thorough washing of the precipitate the excess of alkali is estimated by titrating aliquot portions of the filtrate with standard acid.

424. Estimation of NH_3 in ferrous ammonium sulphate. Use 0·5N. acid and 0·5N. alkali. Fit up the apparatus shown in the sketch (Fig. 74). Crush and dry the salt. Weigh into the flask *A*, an amount sufficient to produce enough ammonia to neutralise about 20 c.c. of the acid. Place in the flask *B*, 25 c.c. of the standard acid. Add a small excess of alkali to the salt and keep boiling for about 20 minutes. The arrangement of the flasks *B* and *C* prevents the acid from rushing back into *A*. Keep the flasks *B* and *C* cool with water. Wash the contents into one flask and titrate the excess of acid with standard alkali. Subtract the volume

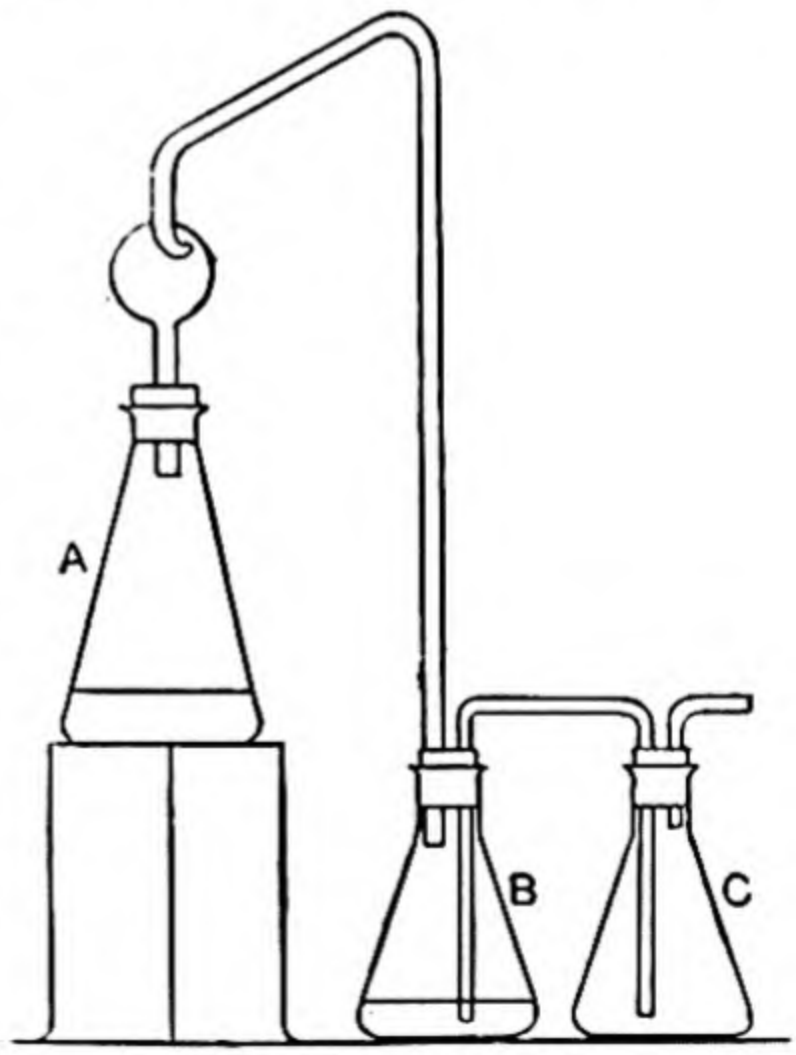


FIG. 74.

required from 25 c.c. to obtain the volume of acid neutralised by the ammonia.

1 c.c. 0·5N. acid = 1 c.c. 0·5N. NH_3 = 0·0085 g. NH_3.

If the volume of acid neutralised by the ammonia be 18 c.c., the weight of ammonia in the salt used is $18 \times 0{\cdot}0085$ g. NH_3.

425. Estimation of nitrates. Nitrates and nitrites may be reduced to ammonia in various ways. In an apparatus like the above (Fig. 74) weigh out about 0·5 g. of potassium nitrate into the flask *A*, and dissolve in about 100 c.c. water. Add 2·5 g. of Devarda's alloy which has been passed through a 60-mesh sieve, and 5 c.c. of alcohol. In the absorption flasks place 25 c.c. of 0·5N. acid, and then to *A* add a solution of 10–12 g. caustic soda in about 100 c.c. water, and quickly close the flask. Warm gently until the reaction begins, and then allow to stand until, in about an hour, the evolution of hydrogen is nearly over. The reduction of the nitrate to ammonia will now be complete, and the liquid in *A* is boiled for 20-30 minutes. The subsequent procedure is the same as for the estimation of ammonia.

426. Estimation of $NaNO_2$ in sodium nitrite. Hydroxylamine and nitrous acid decompose each other readily at moderate temperatures, nitrous oxide being evolved. When the hydrochloride is mixed with sodium nitrite, the following reactions take place :

$$NH_2OH \,.\, HCl + NaNO_2 = NaCl + N_2O + 2H_2O.$$

Prepare roughly a 1 per cent. solution of hydroxylamine hydrochloride, and titrate 25 c.c. with 0·1N. NaOH, using phenolphthalein as indicator :

$$NH_2OH \,.\, HCl + NaOH = NH_2OH + NaCl + H_2O.$$

Weigh out accurately about 1·5 g. of sodium nitrite, dissolve in boiled-out distilled water and make up to 250 c.c. Of this take 25 c.c. for each titration, add 25 c.c. of the hydroxylamine solution, and heat to about 80° for 10 minutes, or until no more nitrous oxide is given off on shaking.

Cool, and titrate the excess of hydrochloride in the solution with 0·1N. NaOH. From the decrease in acidity calculate the

percentage of $NaNO_2$ in the sample of nitrite. Compare with the $KMnO_4$ method (443).

427. Estimation of formaldehyde. A. Formaldehyde is oxidised to formic acid by means of hydrogen peroxide in presence of alkali. The quantity of alkali neutralised thus gives a measure of the amount of formaldehyde. Other acids, of course, must be absent, or if present must be determined by a blank test.

Weigh about 5 g. of the formalin in a weighing bottle, transfer to a 250 c.c. measuring flask, and rinse the bottle several times with a few c.c. of cold water. Now add 100 c.c. of normal sodium hydroxide solution, and very carefully add 50–75 c.c. of hydrogen peroxide solution from a pipette. Mix well and allow to stand in a warm place for $\frac{1}{2}$–1 hour. Make up to the mark with water, and titrate the excess of alkali, with methyl orange as indicator.

The reaction is more rapid with 2N. alkali, and may then require only 10–15 minutes. The peroxide used is 20 volume, and as this may vary in strength care must be taken to use a sufficient quantity, and also to test it for acidity. Compare the result with that obtained by the following method, and by the iodimetric method (462).

B. Formaldehyde reacts with ammonia or ammonium salts to form hexamethylene tetramine (urotropine), the acid being set free :

$$6CH_2O + 4NH_4Cl \rightarrow (CH_2)_6N_4 + 4HCl + 6H_2O.$$

Place 5 c.c. of formalin and a solution of 5 g. NH_4Cl in 50 c.c. water in a small flask, heat to 70–80° and allow to cool. Transfer to a 500 c.c. flask, rinse the small flask several times and make up to the mark. Titrate the free acid with 0·1N. alkali, using methyl orange as indicator. 1 c.c. of the alkali represents 0·0045 g. CH_2O.

428. Determination of the partition coefficient. The distribution of succinic acid between water and ether may be determined in the following way.

Into each of two bottles put 100 c.c. of water and 100 c.c. of ether. To one add 1 g. of powdered succinic acid, to the other

0·5 g. Close the bottles and place them in a thermostat at 20° or 25°, or maintain at room temperature, shaking frequently until equilibrium is reached. Meanwhile prepare a solution of sodium hydroxide approximately .0·05N. With phenolphthalein as indicator, titrate 25 c.c. of each layer.

Let the titration figure for the ether be x and for the water y. Repeat this for the second bottle, and let the figures be x' and y'. It will be found that

$$\frac{x}{y}=\frac{x'}{y'}.$$

The ratio is constant at a given temperature. As explained in par. 52, this is true only when the molecular magnitude is the same in both solvents.

If the solute dissolves as simple molecules in the ether and as aggregates of n molecules in the water, then the constant ratio is $\frac{x}{\sqrt[n]{y}}$ or $\frac{x^n}{y}$.

STANDARD SOLUTIONS OF OXIDISING AGENTS

POTASSIUM PERMANGANATE

429. In presence of a reducing agent, permanganate gives up part of its oxygen, the valency of the manganese changing from 7 to 4 or 2, according as the solution is alkaline or acid. The reactions may be expressed thus :

$$2MnO_4' + H_2O \rightarrow 2MnO_2 + 2OH' + 3\,.\,O,$$
$$2MnO_4' + 6H^{\cdot} \rightarrow 2Mn^{\cdot\cdot} + 3H_2O + 5\,.\,O.$$

In the first case, when no acid is added, hydroxide ions are at once produced and the manganese is precipitated as MnO_2. Each manganese atom gains 3 electrons (94). The reaction tends to be inexact, some manganese forming manganite, $(MnO)MnO_2$, or similar compound (see the estimation of Mn, 436) :

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3\,.\,O.$$

In the second case, in presence of $H^{\cdot}$ ions each manganese atom gains 5 electrons, and the reduction to divalent $Mn^{\cdot\cdot}$ ions is

complete. Sulphuric acid is always used, because it is not itself oxidised, whereas hydrochloric acid tends to liberate chlorine. The metals form sulphates :

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5\,.\,O.$$

Thus $2 \times 158 = 316$ parts by weight of permanganate supply 80 parts by weight of oxygen available for oxidation.

A normal solution of an oxidising agent is one which contains, in one litre, the equivalent weight in grams of oxygen available for oxidation. A normal solution of $KMnO_4$ therefore contains 31·6 g. per litre.

Solutions of about decinormal strength are generally used. The permanganate is its own indicator, one drop giving a perceptible colour in 300–400 c.c. of water.

In such oxidations only the available oxygen need be considered :

$$10Fe^{\cdot\cdot} + 10H^{\cdot} + 5\,.\,O \rightarrow 10Fe^{\cdot\cdot\cdot} + 5H_2O.$$

0·1N. potassium permanganate. Weigh exactly 3·16 g. of the purest potassium permanganate, place it in a small flask and dissolve it by adding successive small quantities of water, rotating gently for a few minutes and transferring carefully to a litre flask. When all is dissolved make up to one litre, and mix well by pouring to and from a dry beaker.

Standardisation of this solution is not quite necessary. It is rendered more stable by the introduction of a little caustic potash (one per cent.) while being prepared. After standing for some time unused it should always be checked. This may be done by titration against pure sodium oxalate, $Na_2C_2O_4$, which is more reliable than crystallised oxalic acid, and may be dried at 120–130°. Weigh accurately 1·5–2 g. of the salt into a 250 c.c. flask, dissolve and make up to the mark. Use 20 c.c. or 25 c.c. for each titration, add 20 c.c. of dilute H_2SO_4, and run in a few drops of permanganate. The reaction

$$2MnO_4' + 5C_2O_4'' + 16H^{\cdot} \rightarrow 2Mn^{\cdot\cdot} + 10CO_2 + 8H_2O$$

proceeds very slowly at room temperature. Heat the titration flask until the colour of the permanganate disappears rapidly,

about 60–80°, and complete the titration at this temperature, adding the last of the permanganate drop by drop. Make three more titrations, and take the average. Correct for the volume of permanganate required to give the end point colour, by adding drops to the same volume of water and dilute H_2SO_4 at the same temperature. Calculate the weight of $Na_2C_2O_4$ oxidised by 1 c.c. of permanganate.

1 c.c. of 0·1N. $KMnO_4$	contains	0·00316 g.	$KMnO_4$.
1 c.c.	,,	,,	yields	0·0008 g.	O.
1 c.c.	,,	,,	oxidises	0·0067 g.	$Na_2C_2O_4$.
1 c.c.	,,	,,	,,	0·0056 g.	Fe.

Should the permanganate prove to be not exactly decinormal, no attempt should be made to correct it, but the normality should be expressed by a factor which is used in all calculations, as in the case of standard acid and alkali (410).

430. Estimation of oxalic acid, $(COOH)_2$, in commercial oxalic acid and oxalates. The method described above for the standardisation of permanganate with sodium oxalate may be used for the estimation of oxalic acid in the crystals, $(COOH)_2 2H_2O$, or in any of its salts. Solutions of approximately decinormal strength should be employed.

The results may be used to calculate the purity of the acid, or of a salt of known composition, or to calculate the equivalent amount of anhydrous acid in the substance.

On the assumption that a salt is pure, the result of the analysis may be used to calculate the number of molecules of water of crystallisation, as in $(NH_4)_2C_2O_4 . H_2O$, or $KHC_2O_4H_2C_2O_4 2H_2O$.

In analysing mixtures of oxalic acid with its salts, the free acid is first determined by titration with standard alkali, using phenolphthalein as indicator, and the total oxalic acid by titration with permanganate.

431. Estimation of Ca in calcium carbonate. Weigh about 0·7 g. of Iceland spar into a beaker, add water and dilute hydrochloric acid, and cover with a clock-glass. When dissolved, dilute

to about 100 c.c., heat nearly to boiling, add a slight excess of ammonium hydroxide, and then a moderate excess of ammonium oxalate. Allow the liquid to settle, filter and wash with hot water until free from soluble oxalate. Make a hole at the bottom of the filter paper and wash as much as possible of the precipitate through into a 250 c.c. flask. Wash the filter paper with warm dilute hydrochloric acid to remove all the oxalate. Add a few c.c. of concentrated sulphuric acid to the liquid, make up to 250 c.c. and titrate 50 c.c. at a time.

1 c.c. 0·1N. $KMnO_4$ = 0·0045 g. $H_2C_2O_4$,
1 c.c. ,, ,, = 0·0020 g. Ca.

All metals that form insoluble oxalates may be estimated in this way. An alternative method is to precipitate the oxalate with a measured excess of standard ammonium oxalate, to reject the precipitate after thorough washing, and determine the excess of oxalate in the filtrate.

432. Estimation of Fe in ferrous ammonium sulphate. Weigh accurately about 4–5 g. of the salt and dissolve in water, adding a few drops of sulphuric acid to prevent hydrolysis. Make up to 250 c.c., take 25 c.c. for each titration, add 25 c.c. dilute sulphuric acid, and run in the permanganate slowly until a permanent colour is obtained. Enter results and calculate as in previous estimations.

433. Estimation of Fe in iron wire. Fit up two small flasks with stoppers and tubes, so that a current of carbon dioxide may be sent through them (Fig. 75). Place the flasks on an iron or asbestos plate, standing on a tripod, and in each place 60–70 c.c. of dilute sulphuric acid. Boil the acid to expel air, and then pass the carbon dioxide through the flasks. Place in each flask about 0·1 g. of iron wire, accurately

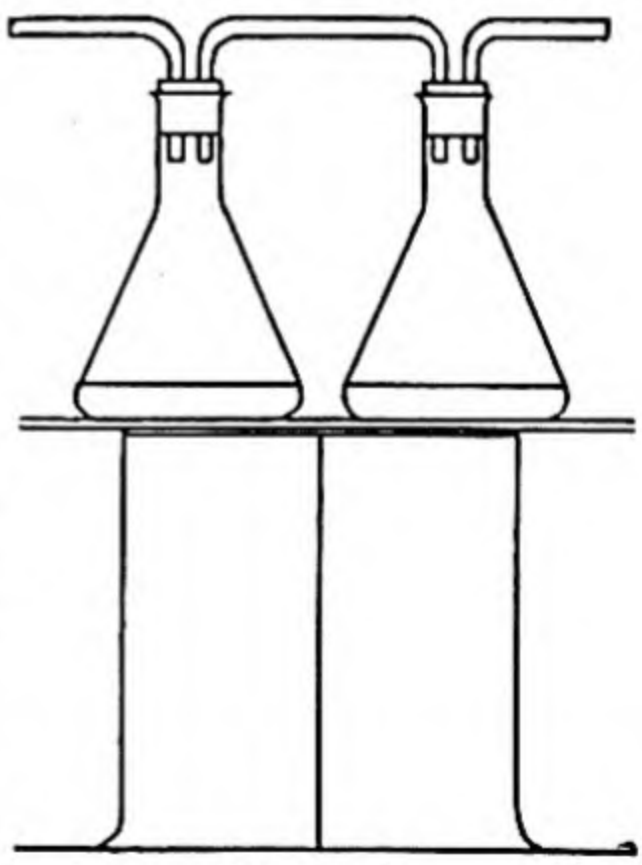


FIG. 75.

weighed, and continue the current of gas until all the iron has dissolved. Titrate the whole of the solution in each flask at one operation, and without loss of time. If the results do not agree, repeat the experiment.

434. Estimation of Fe in iron alum. The iron in this salt is in the ferric state, and must be reduced to the ferrous condition for titration with permanganate.

Weigh accurately into a small flask about 3 g. of iron alum, dissolve in water, add sulphuric acid, and make up to 250 c.c. Place 50 c.c. in the titrating flask, add a few pieces of zinc (free from iron) and allow the action to continue until all the zinc is dissolved. To see whether the reduction is complete, take out a drop on the end of a fine glass rod and touch with it a drop of a solution of potassium thiocyanate on a white plate. If a red colour is produced, more zinc, and possibly acid, must be introduced. If the reduction is found complete, titrate the whole as soon as the zinc has dissolved. While this reduction is proceeding the student should try the action of other reducing agents, as sulphuretted hydrogen or sulphur dioxide, taking care that none of the reducing agent is left before titrating.

435. Estimation of Fe in haematite. Grind the haematite very finely in an agate mortar. Weigh accurately about 1 g. and dissolve in concentrated hydrochloric acid on a water-bath. Reduce the iron to the ferrous state by adding stannous chloride in slight excess. Remove the excess of stannous chloride by adding excess of mercuric chloride solution. Dilute to 250 c.c. and titrate 50 c.c. at a time.

436. Estimation of Mn in manganous salts. As already indicated (429), permanganate in neutral or alkaline solution is reduced only to MnO_2, in which the metal is quadrivalent. If the reducing agent is a manganous salt, the ion is oxidised from $Mn^{\cdot\cdot}$ to $Mn^{\cdot\cdot\cdot\cdot}$, and this also is precipitated as MnO_2:

$$2MnO_4' + 3Mn^{\cdot\cdot} + 2H_2O \rightarrow 5MnO_2 + 4H^{\cdot}.$$

The precipitate is more or less hydrated, to H_2MnO_3, which is manganous acid. This tends to unite with divalent ions of man-

ganese or other metal, forming such compounds as $Mn(HMnO_3)_2$ or $MnO \cdot 2MnO_2 \cdot H_2O$. Volhard added a zinc salt to supply the divalent ions in such manganites, and thus rendered the method an exact one for the estimation of $Mn^{\cdot\cdot}$: all the manganese is precipitated as MnO_2 as expressed in the equation. Thus 1 c.c. of 0·1N. $KMnO_4$ oxidises 0·00165 g. Mn.

The oxalate value of the permanganate may be used, taking $5H_2C_2O_4 \equiv 3Mn$, but it is more satisfactory to standardise the solution against pure manganous sulphate. The crystallised salt has usually five molecules of water, but as this sulphate may crystallise with 1, 3, 4, 5 or 7 H_2O, it is better to use the colourless anhydrous salt obtained by heating to a constant weight at 400°. Weigh accurately 1–1·3 g., dissolve in water, adding a few drops of dilute H_2SO_4, and make up to 250 c.c. Take 25 c.c. for the titration, add 25 c.c. of a 20–25 per cent. $ZnSO_4$ solution, and a few drops of dilute HCl. Heat the solution to boiling and add $KMnO_4$ a few c.c. at a time until in excess. The precipitated MnO_2 renders the end point obscure, but it settles quickly on shaking, and the colour of the solution can easily be seen against the light. For the second titration add nearly as much $KMnO_4$ at once as the first required, finishing carefully, and so also with others until the correct value is found.

Other manganese compounds may be estimated similarly. If iron is present, as in manganiferous ores, it is first oxidised and precipitated as hydroxide by the careful addition of a suspension of ZnO, the liquid made up to a definite volume, filtered through a dry filter, and the filtrate titrated as described above.

437. Estimation of formic acid. This is another example of the use of alkaline permanganate. Formic acid is oxidised very slowly in acid solution, but quite readily in hot alkaline solution :

$$2MnO_4' + 3HCOO' + H_2O \rightarrow 2MnO_2 + 5OH' + 3CO_2.$$

Weigh accurately 0·3–0·5 g. of pure formic acid, or an equivalent quantity of the sample, in a stoppered weighing bottle, dilute with water and make up to 250 c.c. Use 25 c.c. for the titration, add 5 c.c. of sodium carbonate solution, heat nearly to boiling

and run in permanganate until the supernatant liquid has a slight permanent pink colour.

1 c.c. 0·1N. $KMnO_4$ oxidises 0·00138 g. HCOOH.

438. Estimation of hydrogen peroxide. Measure 5 c.c. of 20 volume hydrogen peroxide solution (or 10 c.c. of 10 volume) into a 250 c.c. flask, make up to the mark, and titrate 25 c.c. at a time with permanganate, adding a little dilute sulphuric acid. The reaction is practically instantaneous (see permanganates), and the end point is quite sharp. The calculation is simple :

1 c.c. of 0·1N. permanganate = 0·56 c.c. or 0·0008 g. oxygen
= 0·0017 g. H_2O_2.

For the gas-volumetric method, see par. 558.

439. Analysis of peroxides. A. **Sodium peroxide.** When sodium peroxide is added to very cold dilute sulphuric acid, hydrogen peroxide is produced. To avoid loss of active oxygen the following procedure should be adopted. A solution of 5 g. pure boric acid and 5 c.c. conc. H_2SO_4 in 100 c.c. water is thoroughly cooled, and to this 0·5 g. of sodium peroxide is slowly added, with frequent shaking. The H_2O_2 thus formed is at once titrated with permanganate.

B. **Barium peroxide.** Weigh 0·2–0·3 g. of BaO_2 into the titrating flask and add 100 c.c. of cold water. Decompose the barium peroxide by the gradual addition, with constant shaking, of 20 c.c. of dilute HCl. This acid is used because H_2SO_4 would tend to form a film of $BaSO_4$ on the particles of BaO_2 and prevent complete reaction. When all the barium peroxide is dissolved, titrate the whole solution at once with permanganate.

1 c.c. 0·1N. $KMnO_4$ = 0·00847 g. BaO_2.

440. Analysis of persulphates. These may be estimated by means of their oxidising action on ferrous salts in presence of sulphuric acid :

$$K_2S_2O_8 + 2FeSO_4 \xrightarrow[H_2SO_4]{} Fe_2(SO_4)_3 + K_2SO_4.$$

Prepare a solution of 20 g. crystallised ferrous sulphate and 50 c.c. sulphuric acid, made up to 500 c.c. Weigh out accurately

0·3–0·4 g. of potassium or ammonium persulphate into a flask fitted with wash-bottle tubes, and pass a current of CO_2 through the flask to displace the air. Introduce 25 c.c. of the ferrous sulphate solution, and then 150 c.c. of hot water from which the air has just been boiled out. Mix well until all the persulphate has dissolved, then cool and titrate the solution with 0·1N. permanganate. Titrate also 25 c.c. of the original ferrous sulphate solution, and from the difference calculate the purity of the persulphate.

441. Analysis of percarbonate. Potassium percarbonate decomposes when its aqueous solution is warmed (352). It may be estimated in *cold* solutions by careful decomposition with cold dilute acid :

$$K_2C_2O_6 + 2H_2SO_4 = 2KHSO_4 + 2CO_2 + H_2O_2.$$

Weigh 0·2–0·3 g. of potassium percarbonate into the titrating flask, add 100 c.c. of cold water, and decompose the salt by slowly adding 25 c.c. of dilute (2N.) sulphuric acid. Titrate the H_2O_2 at once. 1 c.c. 0·1N. $KMnO_4 = 0·0099$ g. $K_2C_2O_6$.

442. Estimation of MnO_2 in pyrolusite. A. This may be estimated by a method similar to that used for persulphates. It has the same oxidising action on ferrous salts :

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O.$$

Grind some of the ore to an impalpable powder, and weigh accurately 0·2–0·3 g. into the flask fitted with wash-bottle tubes, and pass CO_2 as in the last experiment. Add 25 c.c. of the ferrous sulphate solution, and while the current of CO_2 is still passing, heat just to boiling until no trace of MnO_2 remains. Cool the flask and titrate the excess of ferrous salt with permanganate. Compare this with 25 c.c. of the original ferrous sulphate, and from the difference calculate the amount of MnO_2.

B. Another method, simple and rapid, makes use of the fact that manganese dioxide and hydrogen peroxide decompose each other in equivalent quantities, in presence of cold dilute sulphuric acid :

$$MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + 2H_2O + O_2.$$

Weigh 0·3–0·4 g. of the finely powdered mineral into a 250 c.c. measuring flask, add 50 c.c. of dilute (2N.) sulphuric acid, and 10 c.c. of 20 volume hydrogen peroxide. The manganese dioxide dissolves completely on mixing, leaving only a slightly coloured insoluble residue. Make up to the mark with water and titrate the excess of H_2O_2 with 0·1N. $KMnO_4$. Estimate the peroxide similarly in the original 20 volume solution. Of the difference in the total volume of permanganate used, each 1 c.c. = 0·00435 g. MnO_2. Compare the gas-volumetric method, par. 559.

443. Estimation of $NaNO_2$ in sodium nitrite. Nitrites are decomposed by dilute acids, nitrous acid being liberated. The nitrous acid is extremely unstable, and even in dilute solutions splits up, liberating nitric oxide :

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The production of nitric oxide (red NO_2 with air) would mean loss of nitrous acid. The estimation should be carried out as follows :

Weigh out about 2 g. of sodium nitrite, dissolve in water, and make up to 500 c.c. Take 25 c.c. for each titration. With the first 25 c.c. run in about 10 c.c. of the permanganate, add a few drops of dilute sulphuric acid, and shake. The colour of the permanganate disappears. Now run in more permanganate (with addition of sulphuric acid if necessary) till a permanent colour is produced. The reduction near the end of the action is slow, and the solution must be allowed to stand. When finished read the burette.

Take another 25 c.c. and run in nearly the volume of permanganate used in the first titration. Add a little acid and run in permanganate till the oxidation is complete. The smell of the contents of the flask will indicate whether there is loss of nitric oxide. Repeat the experiment and obtain three results which agree.

$$\underset{69}{NaNO_2} + \underset{16}{O} = NaNO_3.$$

1 c.c. 0·1N. $KMnO_4$ = 0·0008 g. O ;

$\therefore$ 1 c.c. 0·1N. $KMnO_4$ = 0·00345 g. $NaNO_2$.

444. Solubility determinations by titration. The solubility of any substance which can be titrated with a standard solution can be found by filtering a suitable quantity of its saturated solution, at room temperature, through a dried filter paper into a weighed beaker and again weighing the beaker. The solution is then washed into a 250 c.c. flask, made up to the mark, and 25 c.c. used for each titration.

For other temperatures, saturated solutions are made as in par. 8.

Find the solubility of sodium carbonate, using standard acid; the solubility of oxalic acid or oxalates, using permanganate; and the solubility of a halide, using silver nitrate.

POTASSIUM DICHROMATE

445. Like potassium permanganate, this substance is an oxidising agent, and from each molecule of the salt, three atoms of oxygen are available for oxidation:

$$\underset{294}{K_2Cr_2O_7} + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + \underset{48}{3O}.$$

Hence 294 g. of potassium dichromate yield 48 g. of oxygen available for oxidation, and therefore a normal solution will contain 49 g. of the salt per litre. A decinormal solution (4·9 g. per litre) is generally used.

0·1N. potassium dichromate. Gently fuse a little over 5 g. of pure potassium dichromate in a porcelain dish and then powder in a dry mortar. Weigh out exactly 4·9 g., dissolve in water, and make up to one litre.

1 c.c. 0·1N. $K_2Cr_2O_7$ contains 0·0049 g. $K_2Cr_2O_7$;
$\therefore$ 1 c.c. ,, ,, yields 0·0008 g. O;
$\therefore$ 1 c.c. ,, ,, will oxidise 0·0056 g. Fe.

The estimations of iron are carried out as with permanganate, except in the indication of the end point. With potassium dichromate the reduced solution, which contains chromium sulphate, is green in colour, and it is impossible to distinguish the colour produced by one drop of potassium dichromate in this

liquid. The indicator may be an external one or an internal one.

External indicator. Place a small crystal of potassium ferricyanide in a test-tube, and wash it several times with water; then add water to make a very dilute solution. By means of a glass rod place a series of drops of this solution on a white tile or plate, and from time to time during the titration with the dichromate, take from the flask, on the end of a glass rod, a little of the solution and touch with it one of the drops. If much ferrous iron is present, a strong blue colour will be produced. This will become fainter as more dichromate is added, and finally the drop will give only a faint brown colour. The oxidation is then complete.

Internal indicator. The tedious method involved in the use of ferricyanide as external indicator is avoided by the addition of diphenylamine to the solution to be oxidised. This substance, in presence of a very slight excess of dichromate, gives a deep blue oxidation product. The diphenylamine is used in 1 per cent. solution in sulphuric acid, and 3 or 4 drops are added in each titration. To the ferrous solution are added first 50 c.c. of a solution containing 50 c.c. of syrupy phosphoric acid and 200 c.c. of concentrated sulphuric acid per litre. The iron solution is then diluted to about 150 c.c., the indicator added, and the standard dichromate run in until the last drop causes a change from the green colour of the chromium sulphate to an intense blue. The phosphoric acid (or a fluoride) diminishes the colour of the ferric ion.* The results, although more accurate than those obtained with the external indicator, are a little high. A correction may be applied by adding the dichromate to a solution exactly similar but with no iron salt, until the same deep blue colour is produced. This usually requires about 0·05 c.c., which should be deducted from the titration.

Diphenylamine sulphonic acid may be used in presence of mercuric or tungstate ions, which prevent the development of colour from the base itself. These indicators are useful also in many other oxidation-reduction titrations.

* See Glasstone, *C.S. Annual Reports*, 1934, 305.

446. Estimation of Fe in ferrous ammonium sulphate. Carry out the experiment as with potassium permanganate, but compare the use of the internal indicator with that of the external indicator by making three titrations with each. Calculate as with permanganate.

447. Estimation of Fe in spathic iron ore. Grind the ore very finely. Weigh accurately about 0·5 g. and dissolve in the apparatus used for the estimation of iron in wire (**433**), using a mixture of equal volumes of concentrated hydrochloric acid and water. Dilute with air-free water to five times the volume, and titrate the whole at once with potassium dichromate.

By this process the ferrous iron alone is estimated.

To estimate the *total* iron, take a similar weight of ore, dissolve as before, but there is no necessity to take precautions against oxidation. Do not use much hydrochloric acid in either process, or chlorine may be liberated by interaction with the dichromate.

When dissolved, add 10–15 c.c. of concentrated sulphuric acid ; add some zinc and reduce as with haematite (**435**). Titrate the whole at once. Calculate the ferrous iron as FeO and the ferric as Fe_2O_3.

448. Valuation of zinc dust. This material is used largely as a reducing agent, and its value for this purpose depends on the amount of metallic zinc present. It usually contains, however, a large proportion of zinc oxide, together with other impurities.

A method for its valuation is based on the reduction of potassium dichromate. Weigh out accurately about 0·5 g. of zinc dust into a 250 c.c. flask, and add 50 c.c. of 0·5N. $K_2Cr_2O_7$. Now add dilute sulphuric acid, little by little, with gentle shaking, until the zinc has completely dissolved, and make up to the mark with water. If no reduction had occurred the dichromate solution would now be decinormal. Fill a burette with this solution, and titrate it against 10 c.c. of 0·1N. ferrous ammonium sulphate solution.

Let the weight of the zinc dust taken be 0·57 g., and the volume of dichromate used for each titration be 18·5 c.c. Then (18·5 – 10)

c.c. of 0·1N. $K_2Cr_2O_7$ must have been reduced from every 18·5 c.c. As 1 c.c. of 0·1N. $K_2Cr_2O_7$ is reduced by 0·00327 g. of zinc (32·7 being the equivalent of zinc), the weight of zinc in the 0·57 g. of zinc dust is $\frac{8·5}{18·5} \times 250 \times 0·00327$ g.

$$\therefore \text{ the amount of zinc} = \frac{8·5}{18·5} \times 250 \times 0·00327 \times \frac{100}{0·57}$$

$$= \underline{66·1} \text{ per cent.}$$

STANDARD IODINE AND THIOSULPHATE

449. The usefulness of iodine in volumetric analysis depends largely upon its reaction with sodium thiosulphate, the iodine combining with part of the sodium. The action is represented by the following equation :

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

By this reaction free iodine may be estimated in any neutral solution.

Iodine gives with starch paste an intensely blue adsorption complex commonly known as iodide of starch. If a solution of sodium thiosulphate is added to starch so coloured, the iodine reacts with the sodium thiosulphate as described above and the blue colour is destroyed. The solutions of iodine and thiosulphate generally used are decinormal, and are prepared as below.

0·1N. iodine and thiosulphate. If we regard the free iodine in solution, the equivalent of iodine being 127, we must dissolve 12·7 g. per litre for a decinormal solution. If we consider the iodine solution as an oxidising agent acting according to the equation,

$$I_2 + H_2O = 2HI + O,$$

we again arrive at the amount 12·7 g. to yield 0·8 g. of oxygen, i.e. a decinormal solution.

Weigh out exactly 12·7 g. of powdered purest resublimed iodine into a litre flask. Add about 20 g. of pure potassium iodide and 200 c.c. of water, and shake until the iodine is dis-

solved. Then make up to a litre. Keep well stoppered and in the dark.

The thiosulphate solution should be equivolumetric with the iodine, and we must therefore weigh out a gram molecule of the salt (see equation) for a normal solution, and one-tenth of this for a decinormal solution, and make up to a litre.

The same value is arrived at if we take the principal reacting element, i.e. the sodium which unites with the iodine.

Weigh out 24·8 g. of the pure salt, $Na_2S_2O_3 . 5H_2O$, into a litre flask, dissolve in water and make up to one litre. Keep well stoppered and in the dark.

Equalisation of the solutions. Take 25 c.c. of the iodine solution and run in thiosulphate from the burette. The colour of the iodine becomes fainter as the reaction proceeds, and when only a very faint yellow colour remains, add starch paste. This immediately forms the deep blue complex. Now add the thiosulphate drop by drop, shaking well after each addition, till the blue colour just disappears. Read the burette. If the solutions have been accurately made with pure substances they will be found equivolumetric. If not, equalise by adding water to the stronger and find the strength of the sodium thiosulphate (and therefore also the iodine) as follows.

450. Standardisation of sodium thiosulphate by means of dichromate. Measure 25 c.c. of 0·1N. potassium dichromate into a titrating flask, add about 2 g. of solid potassium iodide, and then 5 c.c. pure concentrated hydrochloric acid. The latter is oxidised by the dichromate, and the chlorine so obtained liberates its equivalent of iodine. The liquid becomes dark brown in colour, and contains iodine equivalent to that in 25 c.c. of 0·1N. iodine solution. Titrate as before with the thiosulphate, adding starch paste when the free iodine is nearly all removed. Continue the addition of thiosulphate carefully until the blue colour is discharged and a pure green solution is left. With a little practice the end point can be accurately determined.

An accurately standardised 0·1N. permanganate solution may be used instead of dichromate.

If the thiosulphate solution is exactly decinormal, 25 c.c. should be required to react with the iodine liberated by 25 c.c. of dichromate. From the volume actually used, the strength of the thiosulphate can be calculated.

451. Estimation of chlorine in chlorine water. Dissolve 7–8 g. potassium iodide in a little water contained in a 250 c.c. flask. Add 50 c.c. saturated chlorine water, and make up to the mark. Titrate the liberated iodine, using 25 c.c. for each titration. Compare the result with that given in **566.**

452. Estimation of bromine in bromine water. Add 50 c.c. of bromine water to a 250 c.c. flask containing a solution of 10 g. of potassium iodide. Make up to the mark and titrate as with chlorine water.

453. Estimation of copper. When potassium iodide is added to a solution of a copper salt, cuprous iodide is precipitated and an equivalent amount of iodine is liberated :

$$\underset{2\times 63{\cdot}57}{2CuSO_4} + 4KI = Cu_2I_2 + 2K_2SO_4 + \underset{2\times 126{\cdot}92}{I_2}.$$

The free iodine is titrated with decinormal thiosulphate.

1 c.c. 0·1N. $Na_2S_2O_3 = 0{\cdot}01269$ g. $I = 0{\cdot}006357$ g. Cu.

Weigh out 5 g. of crystallised copper sulphate, dissolve in water and make up to 250 c.c. Dissolve 10 g. of potassium iodide in 100 c.c. of water and use 10 c.c. for each titration.

Take 25 c.c. of the copper solution in a conical flask, add the potassium iodide, mix well, and run in the thiosulphate as before, adding starch paste when the free iodine is nearly all removed.

As an additional experiment estimate the percentage of copper in the carbonate, which is basic.

454. Estimation of MnO_2 in commercial manganese dioxide. Grind to very fine powder and weigh about 0·5 g. into a small flask with ground-in delivery tube (Fig. 76). Add 25 c.c. of conc. hydrochloric acid and some small pieces of magnesite, and connect to the U-tubes, the first of which contains 4 g. and the

second 2 g. of potassium iodide dissolved in water. The bulbs should be less than half filled. Heat gently. The chlorine evolved liberates iodine, which remains in solution. At the end of the action, gently boil the liquid in the small flask to drive off

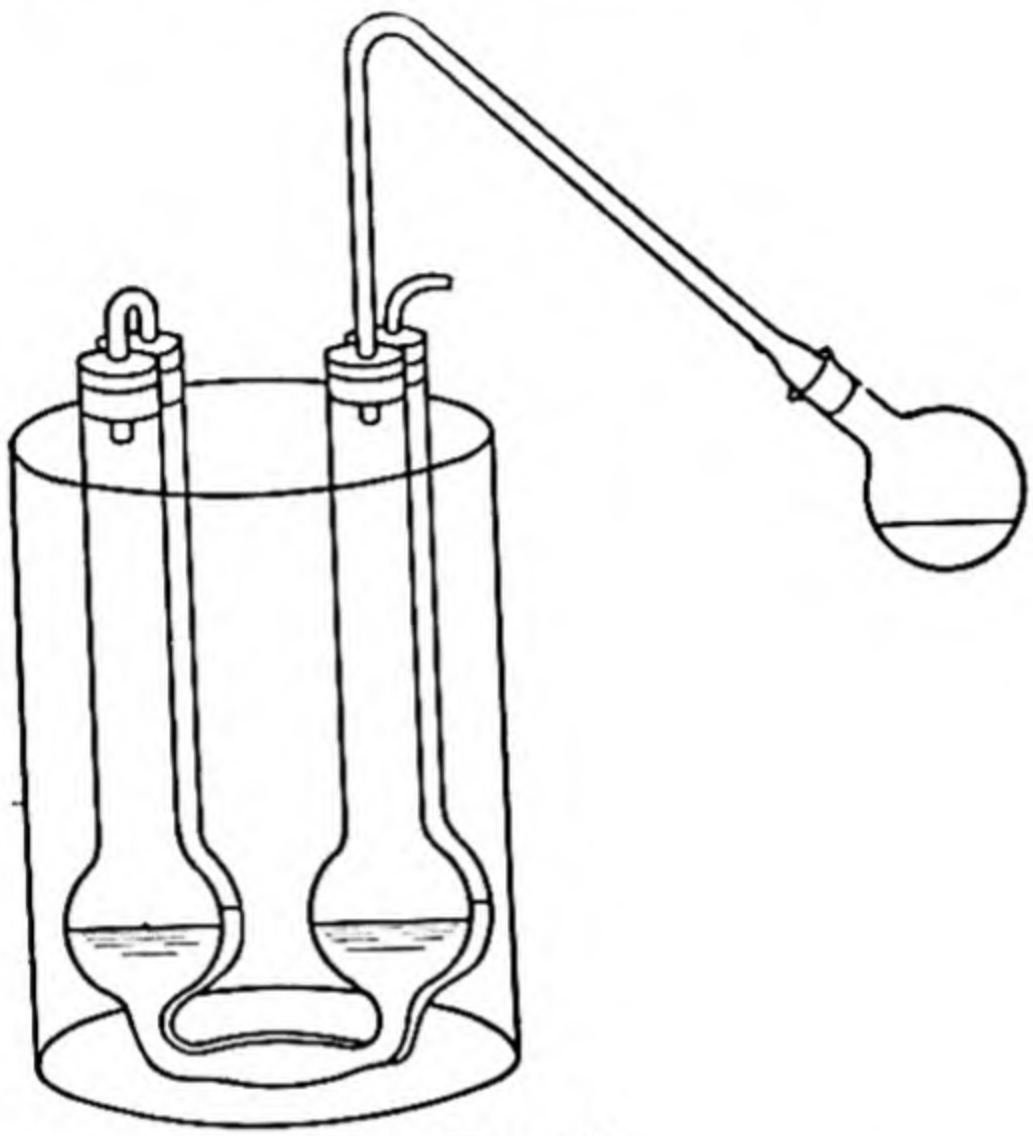


FIG. 76.

the chlorine. The magnesite, which dissolves slowly in hydrochloric acid, is placed in the flask at the beginning of the experiment, in order to provide a stream of carbon dioxide, which prevents the liquid being sucked back, and drives out the chlorine completely.

When the distillation is finished, wash the contents of the U-tubes into a 250 c.c. flask, make up to the mark, and take 50 c.c. for each titration.

$$\underset{86{\cdot}93}{MnO_2} + 4HCl = MnCl_2 + 2H_2O + \underset{2\times 35{\cdot}46}{Cl_2}.$$

1 c.c. 0·1N. $Na_2S_2O_3$ = 0·01269 g. I.

1 c.c. ,, ,, = 0·00435 g. MnO_2.

For the gas-volumetric method, see par. 559.

455. Estimation of available chlorine in bleaching powder. Weigh about 10 g. of bleaching powder into a mortar, add a little water, and grind to a thin cream. Pour the milky liquid into a litre flask and grind the residue with a little more water, and repeat till all the substance is in the flask. Make up to a litre. Shake well, take out 25 c.c., add 10 c.c. of a solution of 5 g. potassium iodide in 100 c.c. of water, and acidify with acetic acid. The liberated chlorine displaces an equivalent quantity of iodine. Titrate with thiosulphate and calculate the amount of chlorine as in previous estimations.

$$Ca\begin{matrix}Cl\\OCl\end{matrix} + 2KI + 2CH_3COOH = I_2 + 2KCl + Ca(C_2H_3O_2)_2 + H_2O.$$

For the gas-volumetric method, see par. 560.

456. Estimation of hypochlorite. Use the solution prepared as directed in par. 116.

Make up the whole solution to 500 c.c. Of this take 10 c.c. and place it in a 250 c.c. flask. Add a solution of 7–8 g. potassium iodide in water, acidify the whole with acetic acid, make up to the mark and mix well. Titrate 50 c.c. at a time with the thiosulphate. From the result calculate the amount of hypochlorite in the original solution.

$$OCl' + 2I' + 2H^{\cdot} = I_2 + Cl' + H_2O.$$

457. Estimation of arsenious and arsenic acids. The first is oxidised to arsenic acid by means of free iodine :

$$AsO_2' + I_2 + 2H_2O = HAsO_4'' + 3H^{\cdot} + 2I'.$$

Weigh out 2 g. of sodium arsenite, dissolve in water and make up to 250 c.c. Measure 25 c.c. of this solution into a titrating flask, add an equal bulk of a saturated solution of sodium bicarbonate to neutralise the hydriodic acid which will be formed, and some starch solution, and titrate with iodine until a permanent blue colour is just obtained.

A similar experiment may be made with sodium arsenate. Weigh out 2 g., dissolve in water, add some acetic acid and boil

for a few minutes to decompose any nitrite in the material. Cool and make up to 250 c.c. Estimate any arsenious acid in the sample by titrating 25 c.c. as above.

To determine the arsenic acid, take 100 c.c. of the solution, reduce by saturating with sulphur dioxide and then boiling off the excess, and make up the cold solution to 200 c.c. Titrate 50 c.c. of this liquid, after adding $NaHCO_3$ and starch, with the iodine solution. This gives the total amount of arsenic, and hence the amount of arsenic acid in the original sample may be calculated.

458. Estimation of antimony. Antimony trioxide may also be oxidised and estimated by means of standard iodine :

$$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI.$$

As in the estimation of arsenic, the hydriodic acid set free must be neutralised with sodium bicarbonate.

Weigh out about 2 g. of tartar emetic, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, dissolve in water, and make up to 250 c.c. Titrate 25 c.c. at a time with standard iodine, after adding an equal bulk of saturated sodium bicarbonate solution and a little starch.

459. Estimation of sulphurous acid in aqueous solution. Measure 5 c.c. of freshly prepared sulphurous acid into a 250 c.c. flask containing 100 c.c. of standard iodine solution. The latter must be in excess, so that the colour is not entirely discharged. Make up to the mark, and titrate the excess of iodine, 50 c.c. at each titration, with thiosulphate.

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$

The estimation may also be made, but less accurately, by diluting 10 c.c. of the sulphurous acid solution to 500 c.c., and running this from a burette into 25 c.c. of the standard iodine.

460. Estimation of sulphurous acid in a soluble sulphite. Weigh about 1 g. of sodium sulphite into a 250 c.c. flask, dissolve in water, acidify with acetic acid and run in a slight excess of iodine solution. Make up to the mark and titrate the excess of iodine with thiosulphate.

461. Estimation of hydrogen sulphide in aqueous solution. Prepare a dilute solution of sulphuretted hydrogen by saturating about 30 c.c. of air-free water with the gas, and diluting 25 c.c. of this to 500 c.c., also with air-free water. Titrate 50 c.c. with iodine in presence of starch until the blue colour appears. The reaction

$$H_2S + I_2 = 2HI + S$$

is not quantitative if more than 0·04 per cent. of hydrogen sulphide is present. If more than this quantity is found, therefore, dilute the solution to a sufficient degree and repeat the experiment. Calculate the solubility of the gas.

462. Estimation of formaldehyde. Formaldehyde is oxidised to formic acid by iodine in alkaline solution, two atoms of iodine being equivalent to one molecule of the aldehyde :

$$H . C'H - O' + I_2 + H_2O \rightarrow H . COO' + 2I' + 3H^{\cdot}.$$

Weigh about 2 g. of the solution (formalin) in a weighing bottle, and make up to 100 c.c. Transfer 10 c.c. to a 250 c.c. measuring flask, add about 25 c.c. of N. NaOH solution, and 75 c.c. of 0·1N. iodine solution, or more if necessary to produce a permanent yellow colour. Mix well and allow to stand for 10–15 minutes. Then add 30 c.c. of normal acid, so that the liquid is just faintly acid, and the excess of iodine is liberated. Make up to the mark and titrate 50 c.c. at a time with thiosulphate.

This method gives good results in the absence of other aldehydes or alcohol, which themselves react with iodine to produce iodoform. Commercial formalin containing only traces of such substances should give the same result by this method as by the peroxide method (427).

463. Estimation of phenol. When a solution of phenol is mixed with bromine water, the insoluble tribromophenol is at once precipitated (285). The excess of bromine can be estimated by adding potassium iodide and titrating the liberated iodine with thiosulphate.

Bromine water is not used, as the bromine is volatile and variable. But a solution of potassium bromate and bromide

liberates bromine when acidified, and in this way an exact standard of bromine can be obtained.

$$KBrO_3 + 5KBr + 6HCl = 3Br_2 + 6KCl + 3H_2O.$$

The bromate must be weighed exactly. Take 2·784 g. and 11–12 g. KBr, dissolve in water and make up to 1 litre. This solution when acidified will liberate bromine to make a 0·1N. solution. It should be checked with 0·1N. thiosulphate solution. 1 c.c. of 0·1N. solution = 0·001567 g. phenol.

Weigh 2–2·5 g. of phenol in a weighed and stoppered weighing bottle, add water to dissolve, transfer and rinse thoroughly into a litre flask, and make up to the mark. Take 25 c.c. for each titration, add 50 c.c. of the bromate-bromide solution and 5 c.c. of concentrated HCl. Mix well and allow to stand for 10–15 minutes. Meanwhile make several similar mixtures, and after the interval complete them in rotation by adding 10 c.c. of a 20 per cent. solution of potassium iodide and titrating with 0·1N. thiosulphate.

If a carbolic acid solution is to be examined, take a suitable volume (or weight), dilute to one litre and proceed as above.

Aniline may be estimated by the same method : it also forms a tribromo-derivative. Determine the solubility of aniline in water at various temperatures. 1 c.c. of 0·1N. thiosulphate = 0·00155 g. aniline.

STANDARD SILVER NITRATE

464. Silver nitrate is used for the titration of soluble halides, the silver halides being quite insoluble in neutral solutions :

$$Ag^{\cdot} + Cl' \rightarrow AgCl.$$

The turbidity of the mixture makes the use of an indicator necessary, and a soluble chromate is generally used. When this is added to a silver solution, red silver chromate is precipitated ; this is decomposed by a soluble chloride, forming silver chloride :

$$Ag_2CrO_4 + 2Cl' \rightarrow 2AgCl + CrO_4''.$$

Thus when silver nitrate solution is run into a solution of a chloride containing two drops of potassium chromate solution,

the permanent red tinge which marks the end point is produced only when the last trace of chloride ion is precipitated. Mineral acids decompose Ag_2CrO_4, and this indicator can therefore be used only in neutral solutions.

465. Adsorption indicators. Certain dyestuffs have the property of forming on the white silver chloride coloured adsorption complexes with silver ions (101). Fluorescein and certain derivatives are examples. If a few drops of a 0·1 per cent. alcoholic solution of fluorescein or of an aqueous solution of its sodium salt be mixed with a chloride solution, no change in the yellowish green dye occurs on adding silver nitrate, until the last trace of chloride ion is precipitated. As soon as silver ions are in slight excess, the red silver fluorescein salt is formed, adsorbed on the silver chloride, which becomes pink. The colour change is sharp, and is at once reversed on addition of a soluble chloride. For very dilute solutions dichlorofluorescein gives better results, with a similar colour change. For bromides, eosin is preferable, and for iodides the best indicator is diiododimethylfluorescein. Fluorescein itself, however, does serve for all.

The halide solutions should be about 0·025N. (25 c.c. of 0·1N. solution diluted to 100 c.c.). Too much indicator tends to obscure the colour change; 4 or 5 drops of the 0·1 per cent. solution for each 100 c.c. should suffice.

466. 0·1N. silver nitrate. Since silver is univalent, the equivalent weight of silver nitrate is the same as the molecular weight; $AgNO_3 = 169·89$ (170). Dissolve exactly 4·25 g. in distilled water, and make up to 250 c.c.

1 c.c. 0·1N. $AgNO_3$	contains	0·017 g. $AgNO_3$,
1 c.c. ,, ,,	precipitates	0·00355 g. Cl,
1 c.c. ,, ,,	decomposes	0·00585 g. NaCl.

467. Estimation of Cl in sodium chloride. Weigh out accurately about 2 g. of pure sodium chloride, dissolve in distilled water and make up to 250 c.c. Take 25 c.c. for each titration and add one or two drops of potassium chromate solution as indicator.

Obtain three concordant results, and then carry out further titrations with fluorescein as indicator.

468. **Estimation of chlorides in tap-water.** Make a centinormal solution of silver nitrate by diluting 25 c.c. of the decinormal solution to 250 c.c. Take 50 c.c. of the water for each titration. Calculate the result in grains per gallon.

1 gallon = 70.000 grains.

70 c.c. of water = 70 g. or 70,000 mg.

Therefore the actual weight in mg. of chloride in 70 c.c. of tap-water will give the number of grains per gallon.

469. **Estimation of mixed chlorides.** Weigh accurately about 2 g. of a mixture of sodium and potassium chlorides, dissolve in distilled water and make up to 250 c.c. Titrate 25 c.c. at a time.

1 c.c. of 0·1N. $AgNO_3$ precipitates 0·00585 g. NaCl,

1 c.c. ,, ,, ,, ,, 0·00745 g. KCl.

Calculate the result as for mixed carbonates (423).

Similar estimations can be carried out with other mixtures of soluble halides, e.g. a mixture of potassium chloride and potassium bromide. In a solution containing hydrochloric acid and sodium chloride the acid would be estimated first by titration with a standard alkali, and the total chloride found in the neutralised solution.

470. **Determination of the equivalent of a metal.** Weigh a suitable quantity of its pure chloride, dissolve in distilled water and make up to 250 c.c. Titrate 25 c.c. at a time with standard silver nitrate. Calculate the weight of chlorine in the chloride, and from this deduce the equivalent of the metal.

STANDARD POTASSIUM CYANIDE

471. Make a solution containing 25 g. of potassium cyanide in 1 litre. Potassium cyanide forms with copper salts a double cupro-cyanide which is colourless; when added to an ammoniacal solution it can be used for the estimation of copper.

To standardise the solution, weigh out exactly 1·25 g. of pure copper into a 250 c.c. flask, and dissolve it in nitric acid (1 : 1) with gentle warming. When dissolved allow the solution to cool and make up to 250 c.c. Take 25 c.c. of the copper solution in a conical flask, and carefully add sodium carbonate until a precipitate just forms. Add just enough ammonia solution (1 : 2) to dissolve the precipitate first formed, and run in the cyanide till the deep blue colour just disappears. Calculate the quantity of water required to make the cyanide solution equivalent to the copper solution, make the addition and titrate again to check the results ; or use a factor, as in the case of standard acid (410).

1 c.c. of the standard cyanide = 0·005 g. copper. The cyanide solution can now be used for the estimation of copper. The conditions under which the cyanide solution is standardised must be adhered to in all estimations, as the reaction is influenced by the concentrations of ammonia and its salts, and by the temperature.

Silver may be estimated by means of standard cyanide. The silver solution is run into the cyanide so long as the AgCN first precipitated redissolves; this continues until one equivalent of silver has been used for each two of cyanide :

$$Ag^{\cdot} + 2CN' \rightarrow [Ag(CN)_2]' ;$$

one more drop of the silver solution then causes a permanent turbidity :

$$[Ag(CN)_2]' + Ag^{\cdot} \rightarrow 2AgCN.$$

This marks the end of the reaction, and thus 1Ag = 2CN.

Usually the silver solution is the standard, and serves for the estimation of unknown cyanide solutions.

STANDARD POTASSIUM THIOCYANATE

472. Potassium thiocyanate gives with solutions of silver salts a white precipitate of silver thiocyanate, insoluble in dilute nitric acid :

$$AgNO_3 + KSCN = AgSCN + KNO_3.$$

The indicator consists of pure iron alum, and is used in presence of nitric acid, which must be free from nitrous acid. To obtain

this, add to the ordinary pure nitric acid one quarter of its bulk of water, and boil till colourless. Since the red ferric thiocyanate is decomposed by soluble silver salts, the silver must be completely precipitated before a permanent red colour is produced. This marks the end point.

0·1N. potassium thiocyanate. Weigh roughly about 10 g. of potassium thiocyanate, dissolve in water and make up to 1 litre. The solution is standardised against decinormal silver nitrate, using the iron indicator.

Take 25 c.c. of decinormal silver nitrate, add 5 c.c. of a saturated solution of iron alum and about 10 c.c. of the pure nitric acid, and run in the thiocyanate until a permanent red tinge is obtained. Repeat the titration, and add to the thiocyanate the quantity of water required to make the solution decinormal.

473. Estimation of silver in a silver coin. Weigh about 0·25 g. of the coin, dissolve in nitric acid, boil to remove nitrous fumes, add the indicator, and titrate with the thiocyanate as before. 1 c.c. 0·1N. thiocyanate = 0·0108 g. Ag.

474. Estimation of copper. When potassium thiocyanate is added to a solution of a copper salt saturated with sulphur dioxide a white precipitate of cuprous thiocyanate is produced.

Weigh out about 0·5 g. of crystallised copper sulphate, dissolve in water in a 250 c.c. flask, pass sulphur dioxide through the solution until saturated, and heat to boiling. Run in the decinormal thiocyanate until its addition produces no further precipitate. Then add 3 or 4 c.c. more and allow to cool. Make up to 250 c.c. and shake well. Filter the solution through a dry filter paper and take 50 c.c. of the filtrate for each titration. Add the indicator as before, run in decinormal silver nitrate till colourless, and titrate the excess of silver nitrate with thiocyanate.

Example.

Bottle and crystals	(1)	17·8902 g.
,, ,,	(2)	17·1599 g.
		0·7303 g.

Thiocyanate added to 250 c.c. = 34·29 c.c.

	Silver nitrate	Thiocyanate	Excess of thiocyanate in 50 c.c.
(1)	2·74	1·67	1·07
(2)	1·16	0·16	1·00
(3)	1·26	0·24	1·02

Excess of thiocyanate added to 250 c.c. = $5 \times 1{\cdot}03 = 5{\cdot}15$ c.c.
Thiocyanate used = $34{\cdot}29 - 5{\cdot}15 = \underline{29{\cdot}14}$ c.c.

$$2CuSO_4 + 2H_2O + SO_2 + 2KSCN = Cu_2(SCN)_2 + 2KHSO_4 + H_2SO_4;$$

$\therefore$ 1 c.c. 0·1N. KSCN = 0·006357 g. Cu.

Percentage of copper in the crystals

$$= \frac{29{\cdot}14 \times 0{\cdot}006357 \times 100}{0{\cdot}7303} = \underline{25{\cdot}33.}$$

475. Estimation of mercury. Solutions of mercuric salts in presence of a large quantity of nitric acid can be titrated with standard thiocyanate :

$$Hg(NO_3)_2 + 2KSCN = Hg(SCN)_2 + 2KNO_3.$$

Weigh 2 g. of mercuric oxide and dissolve it in nitric acid in a beaker. Transfer the solution to a 250 c.c. flask and make up to the mark with water. Take 25 c.c. for each titration, adding in each case 10 c.c. conc. nitric acid, 5 c.c. of the iron alum indicator and 25 c.c. of water. Run in the standard thiocyanate as in the titration of silver solution.

ESTIMATION OF PHOSPHORIC ACID

476. Uranyl salts precipitate pale yellow UO_2HPO_4, from neutral or slightly acid solutions of phosphates (388, 5). In presence of ammonium acetate or hydroxide the precipitate is uranyl ammonium phosphate, $UO_2NH_4PO_4 . 6H_2O$, corresponding with the Mg, Zn or Mn salts, and like them decomposed on ignition, forming uranyl pyrophosphate, $(UO_2)_2P_2O_7$.

The volumetric method is carried out in presence of ammonium acetate, and the end point is indicated by using ferrocyanide

externally, excess of uranium forming the red-brown ferrocyanide. Prepare the following solutions.

Uranyl acetate. Dissolve about 35 g. and make up to 1 litre.

Ammonium acetate. Dissolve 100 g. of this salt and 45 c.c. of glacial acetic acid in water and make up to 1 litre.

Potassium phosphate, KH_2PO_4. Dissolve 19·168 g. to make 1 litre of solution. This corresponds to 10 g. P_2O_5. The solution should be checked by precipitating 25 c.c. with magnesia mixture and weighing the $Mg_2P_2O_7$ (508).

To standardise the uranyl acetate solution, take 50 c.c. of the phosphate solution in a conical flask, with 10 c.c. of ammonium acetate ; add the uranium solution until a drop of the mixture, after thorough shaking, gives a brown precipitate with a drop of saturated ferrocyanide solution on a white tile. Uranyl phosphate is not completely precipitated in the cold ; after boiling, the drop test should no longer give a brown precipitate. More uranium solution is added, and the liquid boiled again, until the exact end point is found. Several titrations must be made.

Alkali phosphate solutions for analysis in this way should be of similar concentration to the KH_2PO_4 solution.

For alkaline earth phosphates the uranium solution should be standardised against a solution of $Ca_3P_2O_8$ in dilute nitric acid.

HARDNESS OF WATER

477. Clark's soap test. Place in a litre flask about 10 g. of sodium oleate or Castile soap, add 500 c.c. of methylated spirit and allow the soap to dissolve. Make up to a litre with distilled water and shake well. To standardise the solution, prepare the following solution of a calcium salt.

Weigh out exactly 1 g. of Iceland spar into a porcelain dish, and add a little dilute hydrochloric acid, covering the vessel with a clock-glass. Allow the substance to dissolve and evaporate to dryness on a water-bath. Redissolve the residue in distilled water and again evaporate, to complete the removal of the hydrochloric acid. Now dissolve the residue in distilled water and make up

to one litre. Each c.c. of this solution contains calcium chloride equivalent to 0·001 g. of calcium carbonate.

Take 20 c.c. of this solution in a stoppered bottle of 250 c.c. capacity and add 50 c.c. of distilled water.

Run in the soap solution from a burette, 1 c.c. at a time, and shake the bottle vigorously after each addition. When a slight lather is obtained add the soap more carefully till a permanent lather is obtained. This lather should last at least two minutes. Read the burette and calculate the volume of water to be added to the soap solution in order that 21 c.c. shall produce a lather with 20 c.c. of the calcium solution. The additional 1 c.c. of soap solution is required to produce a lather with 70 c.c. of distilled water.

The soap solution is now of such strength that 1 c.c. will precipitate 0·001 g. of calcium carbonate or its equivalent.

Since 0·001 g. in 70 c.c. (70 g.) is 1 part in 70,000, the number of milligrams in 70 c.c. is equal to the number of grains per gallon.

With this solution, always use 70 c.c. of the water to be tested, subtract 1 c.c. from the volume of soap solution used, and the remainder will give the number of grains of calcium carbonate present in, or equivalent to the magnesium and other salts present in one gallon. This number represents the hardness of the water in degrees on Clark's scale.

Estimation of the hardness of water. The hardness is distinguished as temporary and permanent, the sum of these being the total hardness. Proceed as follows :

(*a*) *Total hardness.* Take 70 c.c. of water in the stoppered bottle, and titrate with the soap solution. Subtract 1 c.c. from the volume of soap solution used and the remainder gives the number of grains per gallon. Repeat the experiment.

(*b*) *Permanent hardness.* Take about 170 c.c. of the water in a flask and counterpoise on a rough balance. Boil the water for half an hour to remove the temporary hardness. Cool and make the liquid up to its original weight with distilled water, filter through a dry filter paper, take 70 c.c. of the filtrate and titrate as before.

Subtract the permanent hardness from the total hardness, to obtain the temporary hardness.

The soap test for hardness is not very reliable in presence of much magnesium salt.

478. Hehner's method. The following method, which makes use of standard solutions of acid and alkali, is more accurate than that just described. Magnesium salts do not interfere.

Temporary hardness is due to the presence of calcium or magnesium bicarbonates; permanent hardness mainly to calcium or magnesium sulphates or chlorides. The bicarbonates are decomposed by acids:

$$\underbrace{CaCO_3}_{100} . H_2CO_3 + \underset{98}{H_2SO_4} = CaSO_4 + 2H_2CO_3,$$

and may therefore be estimated by the use of standard acids.

The equation indicates that 98 parts of H_2SO_4 are equivalent to 100 parts of $CaCO_3$, or

$$1 \text{ c.c. N} . H_2SO_4 = 0{\cdot}050 \text{ g. } CaCO_3.$$

As the normal acid would be too strong, a certain quantity is diluted to 50 times its bulk to make the solution 0·02N., and 1 c.c. of this corresponds to 0·001 g. $CaCO_3$. If 100 c.c. of the water to be tested are titrated, each c.c. of the acid used will indicate 1 part of $CaCO_3$ in 100,000 parts of water, i.e. 1° of hardness.

Place in a conical flask 100 c.c. of the water, add methyl orange just sufficient to colour it, and run in the acid until the colour changes. The number of c.c. required represents the number of degrees of temporary hardness.

The sulphates and chlorides of calcium and magnesium are decomposed by Na_2CO_3, as also are the bicarbonates:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4,$$

$$CaCO_3 . H_2CO_3 + Na_2CO_3 = CaCO_3 + 2NaHCO_3;$$

but the alkalinity of the solution added is not diminished by the decomposition of the bicarbonates. On this is based the determination of the permanent hardness.

Prepare a 0·02N. Na_2CO_3 solution. Place 100 c.c. of the water to be tested in a platinum dish, add a known excess of the Na_2CO_3 solution, and evaporate the mixture to dryness on the steam-bath. This is necessary in presence of magnesium salts. If these are absent it suffices to boil the mixture for half an hour. The sodium bicarbonate is converted to carbonate during this process. Add water to the residue and filter. Rinse the dish and pass the rinsings also through the filter. Titrate the filtrate, which contains the excess of Na_2CO_3, with 0·02N. H_2SO_4, using methyl orange as before. From the volume of sulphuric acid used, that of the Na_2CO_3 which was necessary to destroy the permanent hardness is found. Each c.c. used represents 0·001 g. of $CaCO_3$ in 100 c.c. of water, or 1 part by weight of $CaCO_3$ in 100,000 parts of the water, i.e. the number of c.c. of Na_2CO_3 used represents the permanent hardness in degrees.

ESTIMATION OF SUGARS

479. The aldehyde and ketone sugars are readily oxidised, and reduce certain metallic salts, especially those of copper, mercury and silver, in alkaline solution. The first is the one most commonly used, and the cupric salt is reduced, in an alkaline tartrate solution, to cuprous oxide. Any sugar which can react with phenylhydrazine will reduce alkaline copper solutions in this way.

The sugar itself is altered in a variety of ways. Glucose is oxidised mainly to tartronic, gluconic, oxalic, acetic and other acids, but partly also changed by the action of the alkali into substances not more highly oxidised than the sugar itself, such as lactic acid. Various other complex substances of aromatic and gummy character are produced. The actual amount of copper reduced is less than half that corresponding with the oxidation of glucose into tartronic acid, which is the chief oxidation product. It is clear that not only is the aldehyde group of glucose oxidised, forming gluconic acid, but also that the alcoholic groups share in the reducing action. Purdie and Irvine * found that the

* *J.C.S.* 1904, 1061.

cupric-reducing power of tetramethylglucose, in which four alcoholic hydroxyl groups are etherified to non-oxidisable methoxyl groups, is only 18·6 per cent. of that of glucose itself.

It is therefore essential to use the materials and to carry out the reaction under strictly standardised conditions. The method was first systematically studied by Fehling,* and is known by his name.

480. Fehling's solution. The materials used for this reagent must be as pure as possible, and the copper solution should be kept separate from the alkaline tartrate. The latter alters slightly in air, and if it is not quite fresh, a blank test should be made before proceeding with the sugar. If any copper is reduced a fresh tartrate solution should be made.

A. **Copper solution.** Dissolve 34·64 g. of pure crystallised copper sulphate in water and make up to 500 c.c.

B. **Alkaline tartrate solution.** Dissolve 175 g. of Rochelle salt and 50 g. of pure sodium hydroxide in water ; cool and make up to 500 c.c.

5 c.c. of each solution are taken for the test, making 10 c.c. of Fehling solution. For complete reduction this is equivalent to :

0·0500 g. of anhydrous dextrose, levulose or invert sugar.
0·0678 g. of dry crystallised lactose, $C_{12}H_{22}O_{11} . H_2O$.
0·0807 g. of anhydrous maltose.

These factors, of course, depend upon strict adherence to the conditions laid down for the experiment.

The substances required for solutions A and B can now be bought, in the above proportions, in tablet form.

481. Estimation of sugar. Place 5 c.c. of each solution in a 6-inch porcelain dish, add 40 c.c. of water and heat to boiling. To the boiling solution, run in from a burette a solution containing about 1 per cent. of the sugar, until after two minutes' boiling the blue colour is completely removed. This shows approximately

* *Ann. Chem.* 1849, **72.** 106.

the amount of sugar solution required to reduce the copper. Now repeat the test, adding the requisite amount of sugar solution all at once to the boiling copper solution. Regulate the flame so that the mixture may begin to boil about one minute after the addition of the sugar, boil for exactly two minutes, and then test the liquid for unreduced copper. This may be done in two ways :

1. Pour a few drops of the liquid into 10 c.c. of starch-potassium iodide solution containing acetic acid. Any unreduced copper causes a separation of iodine, which gives a blue or purple colour with the starch.

2. Filter a few drops of the liquid into a test-tube, acidify with acetic acid, and add a few drops of ferrocyanide. A faint brown or chocolate colour indicates unreduced copper.

Repeat the reduction test until two titrations are recorded differing by only 0·1 or 0·2 c.c., one showing a trace of unreduced copper and the other none. The mean of these two titrations is taken as the volume of sugar solution required to reduce the copper completely.

From this result the amount of sugar in the solution may be easily calculated.

482. Gravimetric estimation of sugar. Greater accuracy may be attained by weighing the cuprous oxide precipitated by a measured volume of the sugar solution from an excess of Fehling's solution. Defren's * method is a convenient one, and may be used for the determination of dextrose, maltose or lactose.

The Fehling's reagent is prepared as above. 15 c.c. of each solution are mixed in a flask and diluted with 50 c.c. of freshly boiled distilled water. The flask is placed in a boiling-water bath for 5 minutes, and then 25 c.c. of the sugar solution (containing about 0·5 per cent. of the sugar) are added and the flask is allowed to stand in the boiling-water bath for 15 minutes. The cuprous oxide is now quickly filtered through asbestos or hardened paper in a Gooch crucible, washed until free from alkali, then quickly dried by subsequent washing with alcohol and ether, and heating to constant weight (half an hour) in the oven.

* *J. Amer. C.S.* 1896, **18.** 749.

The cuprous oxide may also be ignited and weighed as cupric oxide, which Defren recommended, or it may be dissolved in nitric acid and the copper determined electrolytically (545).

From the weight of cupric oxide (W) the amount of sugar may be calculated by Defren's formulae :

$$\text{Dextrose} = W\,(0{\cdot}4400 + 0{\cdot}0_4 37\ W).$$
$$\text{Maltose} = W\,(0{\cdot}7215 + 0{\cdot}0_4 61\ W).$$
$$\text{Lactose} = W\,(0{\cdot}6270 + 0{\cdot}0_4 53\ W).$$

Polarimetric estimation of sugar. The optical rotatory power of solutions of sugar (228) and of other optically active substances may be used to determine the concentration of the substance in a solution. Every such substance has a definite value for the property, which is expressed for the purpose of quantitative comparison in terms of the specific rotation. This depends on various conditions, and is given by the formula :

$$\left[\alpha\right]_\lambda^t = \frac{a}{lw}$$

in which a is the observed angle of rotation, l the length in decimetres of the column of liquid in the polarimeter tube, w the weight of substance in 1 c.c. of the solution, t the temperature of the solution and λ the wave-length of the light used.

The saccharimeter is a modified form of polarimeter intended for the direct estimation of the concentration of sugar solutions. The earliest form was designed by the French physicist Soleil (1848). In such instruments the analyser, like the polariser, is usually fixed, and the rotation produced by a sugar solution is compensated by the movement, across the field, of a wedge of quartz having a rotation opposite in sign to that of the sugar under examination. In this way the field of view is restored to its zero aspect, and the extent of the compensating movement of the quartz, recorded on the graduated disc which actuates it, gives a measure of the concentration of the sugar solution.

SECTION II

GRAVIMETRIC ANALYSIS

GENERAL OPERATIONS

483. Glass and porcelain vessels of various forms are employed in quantitative analysis, beakers or wide-mouthed flasks for precipitation, the latter especially where prolonged boiling is necessary, and porcelain basins usually for evaporations.

It should always be borne in mind that the material of which these vessels are composed is slowly attacked by the fluids employed, even by pure water, but especially by alkaline liquids, small quantities of alkali and silica being removed. Porcelain suffers less corrosion than glass, and should be used for precipitations with alkali, as in the case of zinc carbonate (498, A). A resistant glass having a high silica content, or silica itself, is to be preferred, and in any case it is advisable to fill new vessels with water containing a little sodium carbonate, and boil for an hour or two before use.

484. Precipitation. The remarks already made on this matter (14) apply also to quantitative work. For such work, however, those reactions only are employed in which precipitates of minimum solubility are obtained. Should the solubility be appreciable, the precipitation may be aided by such means as the choice of a suitable temperature, a change in the composition of the solvent, as the addition of alcohol in the precipitation of lead and strontium sulphates (506, 507), the addition of excess of the precipitant or of some other soluble substance having one ion in common with the precipitate, or allowing the liquid to stand for a time sufficient to ensure complete precipitation. This last has the further advantage that many precipitates which are at

first amorphous and bulky, become granular or crystalline on standing, and consequently more dense and more rapidly filtered and washed. It should be remembered, however, that wherever possible a large excess of the precipitant is to be avoided. It sometimes exerts a solvent action on the precipitate, as sodium chloride on silver chloride, and in any case adds to the difficulty of washing, and may thus lead to inaccuracy. The colloidal nature of some precipitates and the appropriate treatment of them should be remembered (101).

485. Filtration. For quantitative work special filter paper must be used, uniform in texture and capable of retaining the precipitate perfectly, and so prepared that the ash left on incineration is reduced to a minimum. Glass funnels should be used, of which the angle is 60° and the stem neither very wide nor very short, and tapering towards the end, which is cut obliquely. The paper should fit closely to the funnel, after moistening with the liquid —water, alcohol, etc.—which is to be filtered, and if it does not, the folding must be modified so as to give the same angle as that of the funnel. The paper also should be of such a size that its edge is about one centimetre below the edge of the funnel, and that it is not more than half filled with the precipitate to be filtered.

Before proceeding to filter, the supernatant liquid, which is usually clear, should be tested with a few drops more of the precipitant, to ascertain that precipitation is complete. The clear liquid is then filtered first, pouring it down a glass rod held vertically and touching the edge of the beaker, which may be slightly greased underneath to help in preventing loss. The precipitate is allowed to remain in the beaker, thoroughly mixed with hot water or other liquid, and again allowed to settle. This washing by decantation may be repeated several times, and then the precipitate is carefully transferred to the filter, using the glass rod. Some of the precipitate will generally adhere to the beaker, and this must be removed with a short piece (1 cm.) of rubber tubing, or a special rubber cap, on the end of the rod.

486. Washing. Perfect washing of the precipitate is of the utmost importance, and defects here are among the most frequent sources of error. It may be done partly be decantation, but must be completed on the filter, the upper edge of which also must be thoroughly washed. If the filter fits closely to the glass, as it should, it may be filled over the edge with the washing liquid without any loss of precipitate. In any case each washing must be allowed to drain away as completely as possible before adding the next (see par. 17) and the washing continued until a few drops of the filtrate collected in a clean test-tube show no trace of the impurities. Amorphous and gelatinous precipitates not only retain much liquid, but also absorb dissolved molecules and ions from the solution (100). They therefore require special care.

The suction filter saves time, but must be used with care, as the washing liquid tends to make channels, which involve imperfect washing. The filter funnel is inserted through a rubber stopper into a suction flask, or other suitable receiver, as in the case of the Gooch filter (Fig. 77). A small platinum cone, or one of hardened filter paper, having the same angle as the funnel, is placed therein, and the paper fitted as usual. Such a filter, properly prepared, will withstand a considerable diminution of pressure without rupture or any loss of the precipitate. The latter becomes less bulky, being compressed into the lower part of the filter, and thus washing is more efficient and the volume of washing liquid is much smaller. The suction may be applied by means of a water pump or other form of pump, or an aspirator.

487. The Gooch filter. This is an asbestos filter, arranged somewhat on the principle of the Soxhlet filter tube, dispensing with the use of paper, and at the same time securing all the advantages of filtration by suction. The Gooch crucible is similar in form and size to an ordinary platinum crucible, and is made in platinum, silica or porcelain, with the bottom full of fine perforations. When ignition is necessary, the crucible may be placed in a non-perforated tray, to protect the contents from direct contact with the flame.

The asbestos employed for the filter must be carefully selected and prepared. It must suffer no loss on treatment with acid or alkaline liquids, or on ignition. To prepare the filter, some fine fibrous silky asbestos is well disintegrated, boiled with hydrochloric acid, then with caustic soda, again with dilute nitric acid, and finally well washed and kept in water in a closed bottle or flask. The crucible is fitted, by means of a broad ring cut from wide rubber tubing, into an ordinary conical funnel, or a cylindrical funnel, which is passed through a rubber stopper into the suction flask (Fig. 77). The pump is set in action, and sufficient of the asbestos fluid carefully poured into the crucible, to leave a thin mat of closely felted fibres. This is thoroughly washed, under continual suction, adding the wash water by means of a beaker and glass rod and not from the wash-bottle, and is then dried, ignited and weighed.

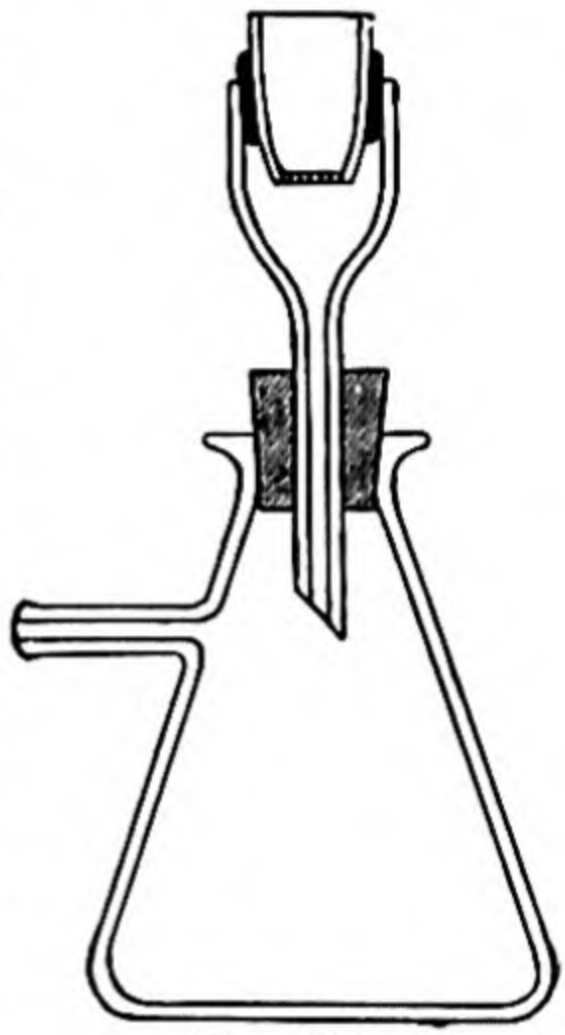


FIG. 77.

The crucible thus prepared is again placed in the funnel, the pump started, and the asbestos moistened with water. The liquid to be filtered is then carefully poured through the filter, and the precipitate added. Continuous suction must be maintained. As a rule, washing by decantation may be dispensed with, and the usual washing completed on the filter, avoiding the use of the wash-bottle. The precipitate is then dried and ignited, and the filter may be used again for several precipitates of the same kind, without renewal.

Instead of the Gooch crucible with its layer of asbestos, a filter disc of fritted glass (16), or a fritted or sintered glass filter crucible can be used. This dispenses with the preparation of the asbestos layer.

488. Drying precipitates. The crucible containing the precipitate is placed in the oven, dust being excluded by covering it closely with a watch-glass or filter paper moistened and folded

round the edges. The steam oven is sufficient to dry most precipitates, especially if they are to be ignited afterwards.

The weighed filter is used in cases in which the precipitate would be altered in an indeterminate manner by ignition, but this method is less accurate than the latter. The crucible is dried in a steam or air bath at the same temperature as that at which the precipitate is afterwards to be dried. Filter papers should be placed in weighing bottles or tubes (Fig. 69), or in paired watch-glasses held together by a wire clip, or in a platinum crucible. The vessel is open while in the oven, is then cooled in the desiccator and closed while weighing. Paper is hygroscopic and must not be exposed to air before weighing. The heating should be continued for an hour in the first instance, and then in half-hour periods until the weight is constant.

Filtration and washing are then proceeded with as usual, the Gooch crucible dried as before, but the paper filter with the precipitate should have a preliminary drying in the funnel, and be then carefully transferred to the vessel already used, and dried to a constant weight. The weight of the precipitate is thus obtained by difference, the actual weight of the paper being unknown and unnecessary.

489. Ignition of the precipitate gives more accurate results than the weighed filter, and is resorted to in the majority of cases, either to ensure complete drying or to convert the precipitate into a more stable product of known composition. The dried precipitate is transferred to a weighed platinum or other crucible, which stands on a sheet of glazed paper, and adhering portions are detached from the filter as completely as possible by gently rubbing the soiled parts of the paper together. Any specks or dust from the precipitate are now swept into the crucible, and the paper is folded along the lines *ab* and *cd* (Fig. 78) so as to keep the

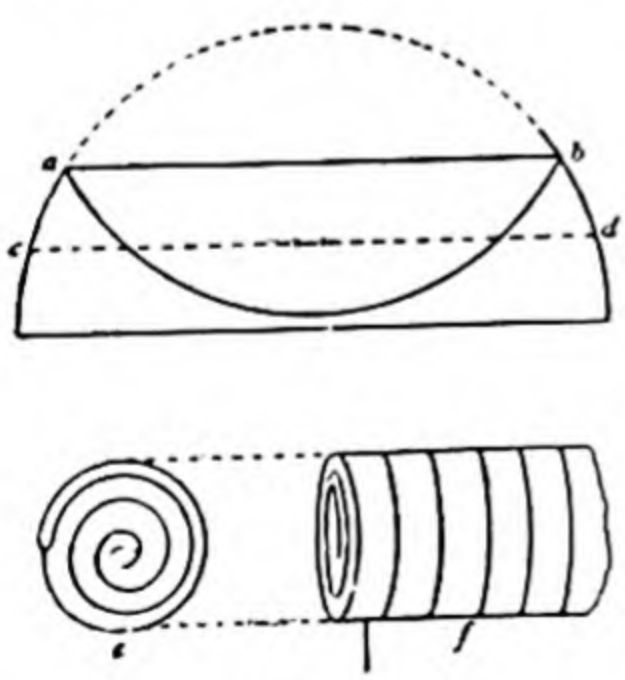


FIG. 78.

soiled part inside, rolled tightly and bound with platinum or nickel-chromium wire. It is then held over the crucible and burned by touching it with the flame, which is at once removed, allowing the paper to burn quietly. The carbonised residue is then touched repeatedly with the flame until the carbon is completely burned. The ash is now dropped into the crucible and the whole ignited to constant weight.

In some cases, such as ferric hydroxide (499), when the precipitate is not affected by contact with the burning paper, the precipitate and paper may be ignited together, even without previous drying. When any reduction takes place, as in the case of copper oxide (491, A), special precautions have to be observed, and corrections applied; these are indicated where necessary.

The **filter ash** is, of course, included with the precipitate on ignition, and its value must be accurately known. This is always printed on the packet, but should be determined by the student himself, by burning six to ten papers in the platinum wire coil as just described (see Fig. 78), or placing them one at a time in the platinum crucible and incinerating to a white ash.

490. **Platinum vessels** must be used with great care, and certain precautions are always to be observed. Platinum is to be preferred to porcelain or silica in that it is a good conductor, quickly heated to redness, and not liable to fracture. But it must never be used in reactions with easily reducible metals, especially those of low melting point like lead and tin, nor in fusions with a strongly alkaline flux, nor with sulphides nor halogen compounds like silver chloride or bromide, nor in any reaction in which halogens are liberated, such as chlorate fusions. During ignition, the crucible should be supported on a triangle of platinum wire, or silica, or failing these, a clean pipe-clay triangle. The crucible must not come in contact with the reducing flame, or unburnt gas, as this causes the destruction of the platinum with formation of a grey carbide, and it must never be touched while hot with brass tongs. After use, the crucible should be cleaned by boiling if necessary with hydrochloric acid or fusing some potassium

bisulphate or borax in it, and after being thoroughly washed, it should finally be polished with moist precipitated chalk.

ESTIMATION OF COPPER

491. A. By precipitation as hydroxide and conversion of this into oxide by ignition. Weigh out accurately 0·8–1 g. of pure copper sulphate, $CuSO_4 . 5H_2O$, into a 500 c.c. beaker, and dissolve in about 100 c.c. distilled water, adding a few drops of dilute HCl. Heat to boiling, and add NaOH solution as long as a precipitate forms. Cover the beaker with a clock-glass, and boil until the precipitate turns black. Allow to settle, test the clear liquid with litmus paper, and if alkaline, filter at once, washing twice by decantation with hot water, and then on the filter, until a few drops of the liquid from the funnel give no turbidity with $BaCl_2$ solution, even on standing for five minutes.

When the precipitate is completely washed, cover the funnel with filter paper, and dry in the steam oven. Transfer the precipitate as completely as possible to a weighed porcelain (or better, platinum) crucible, burn the paper, and let the ash drop into the crucible, first shaking the precipitate to one side. Moisten the ash with two drops of concentrated nitric acid to reoxidise reduced copper, dry gently over a small flame, and then ignite the whole strongly for 15–20 minutes. Allow to cool in the desiccator and weigh. Repeat the ignition until the weight is constant.

The usual method of calculating and entering results is given here as an example.

Bottle and copper sulphate (*a*) -	12·3312 g.
,, ,, ,, (*b*) -	11·4060 g.
Copper sulphate used - - -	0·9252 g.
Crucible, copper oxide and ash (*a*) -	14·1510 g.
,, ,, ,, ,, (*b*) -	14·1510 g.
Crucible - - - - - -	13·8575 g.
Copper oxide and ash - - -	0·2935 g.
Ash - - - - - -	0·0005 g.
Copper oxide - - - - -	0·2930 g.

Now copper oxide is known to contain 63·57 parts of copper in 79·57 of oxide ; therefore the amount of copper in 100 parts of the salt used is given by the expression

$$\text{Cu} = \frac{0{\cdot}2930 \times 63{\cdot}57 \times 100}{79{\cdot}57 \times 0{\cdot}9252} \text{ per cent.} = 25{\cdot}30 \text{ per cent.}$$

$$\text{Theoretically, Cu} = \underline{25{\cdot}46} \text{ per cent.}$$

$$\text{Error} = -0{\cdot}16,$$

$$\text{or } -\frac{0{\cdot}16 \times 100}{25{\cdot}46} = -\underline{0{\cdot}63} \text{ per cent.}$$

B. **By precipitation as cupric sulphide, and conversion of this into cuprous sulphide by ignition with sulphur.** Weigh out and dissolve the copper sulphate as above, add a few drops of HCl (the solution should be free from nitric acid), heat nearly to boiling, and pass H_2S until the liquid is saturated and all the copper precipitated as black CuS. Allow to settle and filter at once. Wash with warm H_2S water until a few drops, on adding HCl and $BaCl_2$, give no turbidity. Keep both filter funnel and beaker covered with clock-glasses during the filtration and washing, to avoid oxidation of the sulphide. Dry the precipitate quickly, transfer to a Rose crucible (Fig. 79), adding the filter ash also, cover the contents of the crucible with powdered sulphur, and ignite in a current of dry hydrogen until all free sulphur is expelled. Allow to cool at first in the current of hydrogen, and when nearly cold place in the desiccator. After weighing, repeat the ignition with sulphur until the weight is constant. The residue is cuprous sulphide, Cu_2S. From the weight of this calculate the amount of copper as above.

FIG. 79.

This method of estimating copper is chiefly employed in separations. The metal may also be precipitated as sulphide by adding $Na_2S_2O_3$ solution, or as cuprous thiocyanate, $Cu_2(SCN)_2$, by adding ammonium thiocyanate in presence of sulphurous acid, with subsequent conversion into Cu_2S by Rose's method. Copper

cannot be precipitated completely as hydroxide in presence of non-volatile organic acids, sugars, etc.

ESTIMATION OF SULPHURIC ACID (SO_4)

492. By precipitation as barium sulphate, $BaSO_4$. Use copper sulphate. Weigh out the salt as above, acidify the solution with hydrochloric acid, heat to boiling and add about 20 c.c. of ammonium chloride solution, to render the subsequent precipitate of $BaSO_4$ more granular and therefore more easily filtered. To the boiling liquid add slowly a boiling solution of $BaCl_2$ as long as a precipitate forms. Allow to settle, wash by decantation several times with hot water, and then on the filter until the water gives no turbidity with $AgNO_3$ solution. Dry, ignite in a platinum or porcelain crucible, and weigh. If much of the precipitate adhered to the filter, moisten the ash with a few drops of HCl, add two drops of H_2SO_4, to convert BaS into $BaSO_4$. Dry carefully, and ignite. Repeat the ignition till the weight is constant. From the weight of $BaSO_4$ calculate the SO_4.

ESTIMATION OF WATER OF CRYSTALLISATION

493. A. In copper sulphate, $CuSO_4 . 5H_2O$. Dry some of the finely powdered salt by pressing between several layers of filter paper, and then leaving it exposed to the air for a short time. Weigh two watch-glasses held with rims together in a wire clip. Place in the glass 1–1·5 g. of the salt and weigh again. Now heat in the air-bath to 120–130° for an hour, separating the glasses meanwhile. Allow to cool in the desiccator, and weigh with the glasses closed. Repeat the heating until the weight is constant. The loss represents $4H_2O$. To determine the remaining molecule of water, heat at 250–260° until a constant weight is obtained. Calculate the percentage in each case.

B. **In zinc sulphate, $ZnSO_4 . 7H_2O$.** This salt loses 6 molecules of water at 100°, the last molecule only at a low red heat. Proceed as above and determine the loss at 120–130°: for the last molecule use a porcelain crucible and heat with the burner to dull redness until the weight is constant.

C. **In barium chloride, $BaCl_2 . 2H_2O$.** This salt loses all its water at 113°. Determine the loss at 120–130°.

A complete analysis of copper sulphate has now been effected. Tabulate the results thus :

	Found	Calculated
Copper (as CuO) - -		25·46
,, (as Cu_2S) - -		(25·46)
SO_4 - - -		38·47
$4H_2O$ - - - -		28·86
$1H_2O$ - - - -		7·21
		100·00

ESTIMATION OF BARIUM

494. By precipitation as barium sulphate. Use crystallised barium chloride. Weigh 0·7–0·8 g. into a 500 c.c. beaker, add a little dilute HCl, heat to boiling and precipitate the $BaSO_4$ by gradual addition of a boiling solution of sulphuric acid or ammonium sulphate. Proceed exactly as in the estimation of SO_4 in copper sulphate. From the weight of $BaSO_4$, calculate the amount of Ba.

Barium may also be estimated as chromate, $BaCrO_4$, but the sulphate method is a better one ; and for the estimation of chromic acid, the lead chromate method is preferable (**501**, B).

ESTIMATION OF CHLORINE

495. By precipitation as silver chloride, AgCl. Weigh 0·5 g. of barium chloride, dissolve in water and acidify with nitric acid. Add a solution of silver nitrate until no more precipitate forms, and then either allow to stand overnight in the dark, or boil gently for fifteen minutes for immediate filtration. The liquid should be protected from strong light. Allow to settle, and filter, washing by decantation with hot water, and then on the filter until free from silver. Dry, and transfer the precipitate to a porcelain crucible, ignite over a small flame till the chloride begins to fuse, and weigh. Burn the filter, place the ash in the

crucible and weigh again. This last increase, less the weight of the ash, gives the weight of silver reduced by the burning of the paper. Calculate the weight of chloride equivalent to this, and add to the weight of the precipitate. Or convert the reduced silver into chloride by placing the ash on the inverted crucible lid, adding two drops of conc. nitric acid to dissolve the silver, and then hydrochloric to reprecipitate as chloride. Dry carefully and ignite until fused. This procedure may be simplified by using the Gooch or sintered glass filter.

This method is a very accurate one. Compare the volumetric estimation of chlorides, etc., by titration with standard silver nitrate (464).

A complete analysis of barium chloride has now been made. Tabulate the results :

	Found	Calculated
Barium - - - -		56·23
Chlorine - - - -		29·02
Water - - - -		14·75
		100·00

Bromides and iodides may be estimated as silver bromide and iodide. The treatment is similar to that of silver chloride, but the Gooch or fritted glass filter should be used and the precipitates dried at 130–150°.

ESTIMATION OF HYDROCYANIC ACID

496. By precipitation as silver cyanide, AgCN, which is weighed. The method is similar to that used for the halogens. Alkali cyanides are deliquescent and must be weighed in closed weighing bottles. If a cyanide solution is to be examined, take a volume equivalent to about 0·2 g. cyanogen, add excess of silver nitrate solution, stir well and acidify with nitric acid. Allow the precipitate to settle, filter through a Gooch filter, dry at 120° and weigh.

Instead of weighing the silver cyanide, it may be decomposed by ignition and the metal weighed.

The volumetric estimation of cyanide by means of standard silver solution is described in par. 471.

ESTIMATION OF SILVER

497. By precipitation as silver chloride. Weigh out 0·5 g. of silver nitrate, dissolve in water and acidify with nitric acid. Precipitate the silver with a slight excess of hydrochloric acid, and complete the estimation as described above for chlorine. From the weight of silver chloride calculate that of the silver present.

ESTIMATION OF ZINC

498. A. By precipitation as zinc carbonate, and conversion of this into oxide, ZnO, by ignition. Weigh about 1 g. of zinc sulphate, $ZnSO_4 . 7H_2O$, into a large porcelain dish, dissolve in about 100 c.c. water, cover the dish with a clock-glass, heat to boiling, and slowly add sodium carbonate solution in excess. Precipitation is not complete in presence of ammonium salts, and these, if present, must be expelled by boiling the liquid containing excess of sodium carbonate. Filter, wash several times by decantation, and then on the filter till free from sodium carbonate. To prevent reduction of ZnO in burning the filter, and consequent loss of zinc by volatilisation, the filter, after removing the precipitate as completely as possible, may be moistened with a strong solution of ammonium nitrate and again dried, and then burned alone. Ignite the whole until the weight is constant, and from the weight of zinc oxide calculate that of the zinc.

B. **By precipitation as zinc sulphide in alkaline solution, and weighing the anhydrous ZnS.** Weigh about 1 g. of zinc sulphate into a 200 c.c. Erlenmeyer flask, dissolve in about 100 c.c. of water, add NH_4OH in slight excess, heat nearly to boiling, and pass a rapid current of H_2S until the liquid is saturated. Nearly fill the flask with water saturated with H_2S, close it with a cork and allow to stand overnight. Filter, wash with water containing ammonium sulphide, and keep the funnel covered with a glass plate.

The dry precipitate is then transferred to a Rose crucible, the filter ash added, the whole covered with powdered sulphur and

ignited in a stream of dry hydrogen. The ignition is repeated with more sulphur until the weight is constant.

ESTIMATION OF IRON

499. By precipitation as ferric hydroxide, $Fe(OH)_3$, and ignition of this to oxide, Fe_2O_3. Weigh about 1·5 g. of ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, dissolve in 100 c.c. water, acidify with sulphuric acid, and add 2–3 c.c. conc. HNO_3. Cover the beaker with a clock-glass, and boil gently for ten minutes to oxidise the iron to ferric salt. When oxidation is complete (ascertain this by mixing a drop of the solution with a drop of freshly prepared ferricyanide solution on a porcelain dish, when there should be no blue colour), add NH_4OH solution in slight excess, heat nearly to boiling, and filter at once, washing by decantation and on the filter until $BaCl_2$ solution produces no turbidity. If ammonium chloride be present in the solution, it must also be completely removed from the precipitate by washing, testing finally with $AgNO_3$ solution. The precipitate, if desired, may be at once ignited in a platinum or porcelain crucible, without previous drying, especially if the suction filter (486) has been used. Careful heating is necessary until the paper is charred, and ignition is then continued at a red heat until the weight is constant.

ESTIMATION OF ALUMINIUM

500. A. By precipitation as hydroxide, $Al(OH)_3$, and ignition of this to the oxide, Al_2O_3. Weigh about 1·5 g. of potash alum, dissolve in 100 c.c. water, add some ammonium chloride solution, and precipitate with a slight excess of NH_4OH. Boil until the excess of ammonia is nearly expelled, and then filter and wash. The precipitate must be strongly ignited, as it retains traces of water to a high temperature. As in the case of iron, previous drying is unnecessary.

B. **By precipitation as 8-Hydroxyquinoline salt.** This organic reagent, under varying conditions, forms insoluble co-ordination compounds with many metals by replacement of the hydrogen

atom of the hydroxyl group. Owing to its high molecular weight the metal forms a small proportion of the precipitate, which is an advantage from the point of view of accuracy. The precipitates are usually crystalline and easily handled, and in some cases afford useful methods of separation. The reagent is known by the trade name " Oxine ".

Weigh 0·3–0·4 g. of potash alum, dissolve in about 100 c.c. of water, add a few drops of dilute HCl and heat to 60–70°. Precipitate the aluminium with an excess of 2 per cent. solution of 8-hydroxyquinoline in 2N. acetic acid, followed by a concentrated solution of 30–40 g. of ammonium acetate. Filter through a Gooch crucible, wash with cold water, dry at 120–130° and weigh. The precipitate is $Al(C_9H_6NO)_3$, and contains 5·871 per cent. of aluminium.

Instead of weighing the precipitate, it may be treated with the standard bromate-bromide solution as described in the estimation of phenol (463). Dissolve the moist precipitate in a little concentrated HCl, dilute with water, add excess of the bromate-bromide solution and sufficient potassium iodide. The organic part of the precipitate is converted into 5 : 7-dibromo–8-hydroxyquinoline. Each c.c. of the bromide solution is equivalent to 0·0002248 g. of aluminium.

ESTIMATION OF CHROMIUM

501. A. By precipitation as hydroxide, $Cr(OH)_3$, and ignition of this to oxide, Cr_2O_3. Weigh out about 1 g. of chrome alum, $Cr_2(SO_4)_3 . K_2SO_4 . 24H_2O$, or about 0·7 g. of potassium dichromate, $K_2Cr_2O_7$, and dissolve in 100 c.c. water. In the latter case, reduce the dichromate completely to chromium salt with sulphurous acid, or by heating with 5 c.c. alcohol and an equal bulk of concentrated HCl, until all alcohol and aldehyde are expelled. Precipitate with NH_4OH in slight excess, and heat until the excess of ammonia is nearly removed and the liquid is quite colourless. Complete the estimation as for iron or aluminium.

B. By precipitation as lead chromate, $PbCrO_4$, which is weighed. This method is described under lead (506 B).

C. **By precipitation as mercurous chromate, Hg_2CrO_4, which is ignited to Cr_2O_3.** Weigh about 1 g. of potassium chromate or dichromate, dissolve in water, and in the case of a dichromate add a little sodium acetate. Precipitate with a solution of mercurous nitrate, allow to settle, filter, and wash the precipitate with a dilute solution of mercurous nitrate. When dry, ignite without burning the paper separately, and weigh the residue of Cr_2O_3.

ESTIMATION OF NICKEL

502. A. **By precipitation as nickelous hydroxide, $Ni(OH)_2$, and conversion of this into oxide, NiO, by ignition.** Weigh about 1 g. of nickel ammonium sulphate, $Ni(NH_4)_2(SO_4)_2 . 6H_2O$, into a 500 c.c. beaker ; dissolve in water, adding a few drops of HCl, precipitate with a slight excess of sodium hydroxide or carbonate, and heat to boiling. Wash by decantation with boiling water several times, boiling at each washing, and then on the filter until $BaCl_2$ produces no turbidity. Dry, and ignite strongly in a platinum or porcelain crucible. The residue is NiO.

This residue may be easily reduced to metallic nickel by Rose's method of heating in a current of hydrogen (491, B). The reduced metal is allowed to cool at first in the current of hydrogen, and the ignition repeated until the weight of metal is constant.

B. **By precipitation as dimethylglyoxime salt,**

$$[HO . N : (C . CH_3)_2 : NO]_2Ni,$$

which is weighed. Weigh 0·5–0·6 g. of nickel ammonium sulphate, dissolve in about 250 c.c. of water, and precipitate the nickel by adding about 50 c.c. of a 1 per cent alcoholic solution of dimethylglyoxime. Make the liquid just alkaline with ammonia, stir well, and warm on the steam for half an hour. Test the clear liquid with a little more of the reagent, filter through a Gooch or fritted glass filter, dry at 120° and weigh.

ESTIMATION OF COBALT

503. A. **By precipitation as hydroxide, and reduction of this to metal, which is weighed.** This is the most accurate method of

determining cobalt. Weigh about 1 g. of cobalt potassium sulphate and proceed as for nickel (502, A). The precipitated hydroxide should be boiled until it is almost black, and weighed as metallic cobalt.

B. **By precipitation as α-nitro–β-naphthol salt.** In this way cobalt may be separated from nickel and zinc, and also from chromium and aluminium. Prepare a solution of cobalt salt with about half the quantity used in A, add 1–2 c.c. of dilute sulphuric acid and 4–5 c.c. of 20 volume H_2O_2; alkalise the liquid with NaOH to produce a slight precipitate of $Co(OH)_3$. Redissolve this precipitate in just enough glacial acetic acid, heat the solution to 50–60°, and precipitate the cobalt by adding the nitronaphthol reagent. This is prepared by dissolving 2 g. in 100 c.c. of glacial acetic acid, adding an equal volume of water and filtering. About 120 c.c. will be required to give a sufficient excess. After standing for half an hour, filter through a Gooch crucible, wash with dilute acetic acid, then with warm water, and dry at 130°. The precipitate is $Co[C_{10}H_6O(NO_2)]_3$, and contains 9·463 per cent. of cobalt.

ESTIMATION OF CALCIUM

504. By precipitation as calcium oxalate, CaC_2O_4, which is converted by ignition into carbonate or oxide. Weigh about 0·5 g. of Iceland spar into a beaker, and dissolve in dilute HCl, covering the beaker with a clock-glass. Boil to expel carbon dioxide, add NH_4OH in excess, and to the hot solution add ammonium oxalate solution as long as a precipitate forms. Boil for twenty minutes, and then allow the precipitate to settle completely. Decant the clear liquid through a filter, wash several times by decantation with hot water, and then on the filter until completely free from oxalate.

Dry the precipitate in the steam oven, place in a platinum or porcelain crucible, burn the filter and place the ash also in the crucible. The oxalate may be converted into carbonate by heating gently over a small flame, so that the bottom of the crucible is scarcely red. It is better, however, with the quantity used above, to convert directly into oxide, CaO, by heating for twenty

minutes over the blowpipe, or with a Méker burner, until the weight is constant. From the weight of calcium oxide calculate that of the calcium.

ESTIMATION OF OXALIC ACID

505. By precipitation as calcium oxalate. Weigh about 0·8 g. of pure ammonium oxalate, $(NH_4)_2C_2O_4 . H_2O$, dissolve in water, add a little acetic acid and heat to boiling. Precipitate calcium oxalate by adding excess of a clear solution of calcium acetate, and treat the precipitate as described above. From the weight of calcium oxide calculate the equivalent amount of (C_2O_4) or of oxalic acid.

ESTIMATION OF LEAD

506. A. By precipitation as sulphate, $PbSO_4$, which is weighed. Weigh about 1 g. of crystallised lead acetate, $Pb(C_2H_3O_2)_2 . 3H_2O$, dissolve in 50–60 c.c. water, and add a little acetic acid. Keep the liquid cold, and add dilute sulphuric acid until no more precipitate forms. Add alcohol equal in bulk to the liquid, mix well, and allow to stand overnight. This ensures complete precipitation of the lead sulphate, which is slightly soluble in water alone. Filter, and wash with 50 per cent. alcohol until all H_2SO_4 is removed.

Place the dry precipitate in a porcelain crucible, burn the filter on the crucible lid, and moisten the ash with two drops HNO_3 and one drop dilute H_2SO_4, to reconvert any reduced lead or PbS into $PbSO_4$. Dry carefully, and ignite the whole to dull redness until the weight is constant.

B. **By precipitation as chromate, $PbCrO_4$, which is weighed.** Weigh about 0·8–1 g. of lead acetate or nitrate, dissolve in water, add a little acetic acid and some sodium acetate solution, and precipitate the lead with excess of potassium chromate. Allow the precipitate to settle, filter through a weighed filter, wash first by decantation with cold water and then on the filter. Dry at 100° until the weight is constant. The residue is $PbCrO_4$.

This method may also be employed for the estimation of chromium.

C. **Lead may also be estimated** as sulphide, PbS, by the method given for copper (in acid solution, **491**, B), or for zinc (in alkaline solution, **498**, B), or as molybdate (**517**, B).

ESTIMATION OF STRONTIUM

507. By precipitation as sulphate, $SrSO_4$, which is weighed. Weigh about 1 g. of strontium carbonate, $SrCO_3$, and dissolve in dilute HCl, covering the beaker with a clock-glass. Add 60–70 c.c. distilled water, and precipitate the strontium as sulphate, as described above for lead (**506**, A). Strontium sulphate is also slightly soluble in water.

Dry the precipitate and ignite it as described for barium sulphate. The residue is $SrSO_4$.

ESTIMATION OF MAGNESIUM

508. A. By precipitation as magnesium ammonium phosphate, $MgNH_4PO_4 . 6H_2O$, and conversion of this by ignition into magnesium pyrophosphate, $Mg_2P_2O_7$. Weigh about 1 g. of magnesium sulphate, $MgSO_4 . 7H_2O$, dissolve in 70–80 c.c. of water, add 25 c.c. of a 20 per cent. solution of ammonium acetate, and an excess of ammonium phosphate. Heat the liquid nearly to boiling, add a little phenolphthalein, and then slowly add dilute NH_4OH solution to the hot mixture until a precipitate begins to form. Stir well until the precipitate becomes crystalline, but avoid contact between the rod and the sides of the beaker. Rinse the rod, add 25 c.c. of concentrated NH_4OH solution, cover the beaker with a clock-glass and allow to stand overnight. In this way pure magnesium ammonium phosphate is obtained. Precipitation in the cold is liable to cause contamination with traces of $Mg_3(PO_4)_2$, or of $Mg(NH_4)_4(PO_4)_2$, according to conditions, the result being low or high in consequence.

Filter, and wash with a mixture of 1 part NH_4OH (0·880) and 3 parts water, the precipitate being slightly soluble in water. Continue washing on the filter until the filtrate gives no turbidity with $AgNO_3$, after acidifying with HNO_3. Dry the precipitate, transfer to a platinum or porcelain crucible, add the filter ash,

and ignite, *gently* at first until water and ammonia are expelled, and then strongly until the weight is constant. The residue is magnesium pyrophosphate, $Mg_2P_2O_7$. From its weight calculate the weight of magnesium.

B. **By precipitation as 8-hydroxyquinoline salt.** Take about 0·5–0·8 g. of magnesium sulphate, dissolve in 60–70 c.c. of water, add NH_4Cl to prevent the precipitation of magnesium hydroxide, and make alkaline with NH_4OH. Heat nearly to boiling and add excess of a 5 per cent. solution of 8-hydroxyquinoline in N. acetic acid. A greenish-yellow precipitate of $Mg(C_9H_6NO)_2 . 4H_2O$ is formed, which becomes crystalline and is easily filtered. Wash with hot water containing a little ammonia, and dry at 105°. The precipitate loses half of the water at this temperature, and the dihydrate contains 6·988 per cent. of Mg.

The calcium salt of oxine is much more soluble, but if calcium be present it is well to dissolve the magnesium compound in dilute HCl, add a little more of the reagent and reprecipitate by adding ammonia.

Instead of weighing the precipitate, it may be dissolved in dilute hydrochloric acid and treated with 0·1N. bromate-bromide solution as described for aluminium (**500, B**). In this case 1 c.c. of the bromate solution is equivalent to 0·000304 g. Mg.

ESTIMATION OF PHOSPHORIC ACID

509. A. By precipitation as magnesium ammonium phosphate. Weigh about 1 g. of sodium phosphate, $Na_2HPO_4 . 12H_2O$, dissolve in 50–60 c.c. of water, add about 1 c.c. of dilute HCl and excess of magnesia mixture (a solution of magnesium sulphate or chloride with NH_4Cl and NH_4OH). Add 25 c.c. of a 20 per cent. solution of ammonium acetate, and a few drops of phenolphthalein. Heat the liquid nearly to boiling, and then slowly add dilute NH_4OH solution until a precipitate begins to form. Proceed as described in **508** A, and weigh as $Mg_2P_2O_7$.

B. **By precipitation as ammonium phosphomolybdate.** When heavy metals or alkaline earths are present in a solution containing phosphoric acid, the latter must be removed in acid solution.

Weigh 1 g. of sodium phosphate, dissolve in 50–60 c.c. of water, add 2–3 c.c. of dilute HNO_3, heat the solution to 60–70°, and add excess of ammonium molybdate solution. Maintain at this temperature for an hour, when the precipitation of the phospho-12-molybdate, $(NH_4)_3PO_4 . 12MoO_3$, will be complete. Filter, wash once by decantation and then on the filter with a N. solution of NH_4NO_3 containing 2N. HNO_3. The precipitate may be treated in one of four ways :

I. Heated to 250–300°, it has the above composition, and contains 3·784 per cent. of P_2O_5.

II. It may be dissolved in a measured excess of standard alkali and the excess titrated with standard acid. 1 c.c. N. NaOH is equivalent to 0·00296 g. P_2O_5.

III. It may be dissolved in excess of NH_4OH, the excess nearly neutralised with HCl and the phosphate precipitated with magnesia mixture as described in A.

IV. It may be converted into lead molybdate, $PbMoO_4$, by the method described in 517 B.

Phosphorous acid, H_3PO_3, and hypophosphorous acid, H_3PO_2, may be estimated by first oxidising to H_3PO_4, by evaporating to a small volume with 5–10 c.c. of concentrated HNO_3, and then estimating the H_3PO_4 as $Mg_2P_2O_7$.

ESTIMATION OF ARSENIC

510. A. The above method may also be used for this purpose. The arsenic must be in the form of arsenate, as sodium arsenate, $Na_2HAsO_4 . 12H_2O$. Arsenious compounds may be oxidised by heating in solution with HCl and a little $KClO_3$. When completely oxidised, make alkaline with ammonia, and precipitate with magnesia mixture in the form of magnesium ammonium arsenate, $MgNH_4AsO_4 . 6H_2O$. Treat the precipitate exactly as the corresponding phosphate, except that it should be heated very gradually, preferably in an electric oven, to about 500°, to avoid reduction by the ammonia and consequent loss of arsenic. When all NH_3 is expelled heat to 800–900° for 10–15 minutes, cool and weigh as pyroarsenate, $Mg_2As_2O_7$. If a gas burner is

used, heat very slowly, and before the higher temperature is reached sprinkle a little powdered NH_4NO_3 over the precipitate, or complete the ignition, with the Rose crucible cover, in a current of dry oxygen.

This method is used for the separation of arsenic from antimony, and also, with a slight modification, from tin.

B. **By precipitation as arsenic trisulphide, As_2S_3, which is weighed.** Weigh about 0·8 g. of sodium arsenite into a 300 c.c. conical flask, dissolve in water, acidify with HCl, and add a few grams of tartaric acid. Fit the flask with a doubly-bored stopper carrying two right-angled tubes, one passing to the bottom of the flask for the supply of sulphuretted hydrogen, and the other ending just beneath the cork, and dipping into water in a second flask. This arrangement protects the liquid in the first flask from air. The arsenic solution is heated nearly to boiling and is then saturated with sulphuretted hydrogen. After standing for some time until the precipitate has settled, the excess of sulphuretted hydrogen is removed from the liquid by passing a current of carbon dioxide gas, and the liquid is then filtered through a weighed filter. After washing with water containing sulphuretted hydrogen until the washings are free from chloride, the precipitate is dried at 100° and weighed.

If the precipitate contains sulphur, it must be converted into arsenic acid by oxidation with conc. HNO_3, and the arsenic then estimated as magnesium pyroarsenate as in method A.

A volumetric method for the estimation of arsenic is given in par. **457.**

ESTIMATION OF ANTIMONY

511. A. By precipitation as antimony trisulphide, Sb_2S_3, which is weighed. Weigh about 1 g. of potassium antimonyl tartrate (tartar emetic), $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, and treat exactly as described for the precipitation of arsenic trisulphide, except that the solution should be kept gently boiling during the latter part of the precipitation with sulphuretted hydrogen. After removing the excess of gas with carbon dioxide, filter through a weighed filter, drv at 100° and weigh.

The precipitate still contains water, and usually also sulphur. Test a small portion of the dried precipitate by boiling with conc. HCl ; if it dissolves completely, no free sulphur is present, and the sulphide must now be rendered perfectly anhydrous. To do this, weigh a portion of the precipitate (dried at 100° and preserved meanwhile in the desiccator) into a porcelain boat. Place this in a glass tube nine or ten inches long, and heat in a current of dry carbon dioxide until the precipitate is quite black. Allow to cool in the current of dry gas, weigh, and repeat the ignition until the weight is constant. If free sulphur is present, the same procedure is adopted, but the temperature must be higher. From this experiment the total weight of Sb_2S_3 in the original precipitate can be calculated, and hence the amount of Sb.

B. **By precipitation as trisulphide, and conversion of this into antimony tetroxide, Sb_2O_4, by oxidation with concentrated nitric acid.** As described above, prepare the antimony trisulphide, filter through a weighed filter, dry at 100° and weigh.

Transfer the bulk of the precipitate, without examining for free sulphur, to a weighed porcelain crucible, and weigh. Moisten with a few drops of dilute HNO_3, keeping the crucible covered, and then carefully add conc. HNO_3, little by little, until the precipitate is just covered. When the reaction subsides, heat gently on the steam until the sulphide is completely oxidised, and then evaporate to dryness. Add a little fuming HNO_3 to complete the oxidation, again evaporate to dryness, and then ignite, gently at first to expel sulphuric acid, and then more strongly, until the weight is constant. The residue is Sb_2O_4. Calculate the weight of this which would have been obtained from the whole of the original precipitate, and from this in turn calculate the antimony.

For a volumetric method, see **458.**

ESTIMATION OF TIN

512. By conversion into stannic oxide, SnO_2, which is weighed.

A. *Treatment of the metal or its alloys with nitric acid.* Weigh about 0·3 g. of tin, in the form of fine powder or foil, into a 250 c.c. Erlenmeyer flask, add 20 c.c. water, and then 50 c.c. conc.

HNO_3 (sp. gr. 1·4). Cover the flask with a watch-glass and keep in the cold until the reaction has subsided. Heat towards the end, adding more HNO_3 if necessary, until the residue of stannic acid is perfectly white. Evaporate nearly to dryness in a porcelain dish to expel most of the nitric acid (chlorides must be absent or loss of tin will result by this method), extract with hot water, filter, wash and dry the precipitate. Transfer to a porcelain crucible, add the ash, and ignite over the blowpipe or Méker burner until the weight is constant. From the weight of SnO_2 calculate that of the tin.

B. *Treatment of solutions of tin.* This may be done as above, in the absence of chlorides, but it is better to oxidise the tin to stannic salt, by warming with HCl and $KClO_3$, and precipitate the tin from this in the form of stannic acid. Carefully neutralise the oxidised solution with ammonia, add a quantity of strong solution of sodium sulphate or ammonium nitrate, and warm on the steam for some time. Stannic sulphate and nitrate are thus completely hydrolysed by water, and the tin is completely precipitated as stannic acid. Filter, wash first by decantation, and then on the filter until free from chlorides, dry, ignite and weigh as SnO_2.

ESTIMATION OF MERCURY

513. A. By precipitating as mercuric sulphide, HgS, which is weighed. Weigh about 0·5 g. of mercuric chloride into a 500 c.c. beaker, dissolve in 150 c.c. water, acidify with HCl, warm gently and saturate with sulphuretted hydrogen. Allow the precipitate to settle, filter through a weighed filter, dry at 100° and weigh.

If the precipitate contains free sulphur, this may be removed by washing the dry precipitate on the filter with carbon disulphide, or by warming it in a porcelain dish with a strong solution of sodium sulphite, and again filtering and washing.

B. **By precipitating as mercurous chloride, Hg_2Cl_2, and weighing as such.** Weigh out a little mercurous nitrate, dissolve in water containing a few drops of dilute HNO_3, and precipitate the mercury with a solution of common salt. Allow to settle, filter

through a weighed filter, wash with water until free from chloride, dry at 100° and weigh.

Mercurous compounds may also be oxidised with aqua regia, and the mercury then estimated as sulphide.

ESTIMATION OF BISMUTH

514. A. By precipitation and weighing as phosphate, $BiPO_4$. Weigh 0·3–0·5 g. of bismuth oxide, Bi_2O_3, into a beaker, and dissolve in dilute nitric acid. Neutralise the excess of acid by adding NH_4OH carefully until a slight permanent precipitate of $Bi(OH)_3$ is formed, and then add dilute HNO_3 until this is just redissolved. Heat the solution to boiling, and while stirring add an excess of a 20 per cent. solution of ammonium phosphate. Allow the precipitate to stand for half an hour, filter through a Gooch crucible and wash with water containing 2–3 per cent. of NH_4NO_3 and a very little HNO_3. Ignite the Gooch gently inside another crucible, and weigh the $BiPO_4$.

The bismuth solution should not contain chloride or sulphate, as these are liable to yield basic salts which do not change to phosphate, or to oxide in method B.

B. **By precipitation as carbonate, and ignition of this to the oxide, Bi_2O_3.** Weigh 0·5 g. of bismuth oxide or carbonate, dissolve in a little nitric acid, and dilute with water. Add ammonium carbonate in excess, and heat nearly to boiling for about half an hour. Allow the precipitate to settle, filter and wash, dry, ignite and weigh the residue of Bi_2O_3.

ESTIMATION OF CADMIUM

515. A. By precipitation as carbonate, and ignition of this to oxide, CdO. Weigh about 0·8 g. of the sulphate, $3CdSO_4 . 8H_2O$, or 0·6 g. cadmium carbonate, $CdCO_3$, dissolve in water or dilute HCl in a 500 c.c. porcelain dish, and proceed with the experiment exactly as described for the estimation of zinc as oxide (498, A). The residue is CdO.

B. **By precipitating as sulphide, CdS, and weighing in this form.** Weigh out and dissolve the cadmium salt as above, and nearly

neutralise the liquid with sodium carbonate. Precipitate the cadmium by saturating the warm solution with sulphuretted hydrogen, allow the precipitate to settle and filter through a weighed filter. Wash with water containing sulphuretted hydrogen, keeping the funnel covered with a clock-glass to prevent contact of the precipitate with air as far as possible, dry at 100° and weigh. If the precipitate contains free sulphur, this may be removed by the methods given for mercury sulphide (513, A).

ESTIMATION OF MANGANESE

516. A. **By precipitation as carbonate, $MnCO_3$, which is converted by ignition into trimanganic tetroxide, Mn_3O_4.** Weigh about 0·8 g. of manganous sulphate, $MnSO_4 . 5H_2O$, and dissolve in water, precipitate with sodium carbonate and filter, exactly as described for zinc (498 A). The manganese is not completely precipitated, however, and the filtrate and the first two washings must therefore be evaporated to dryness. The residue is extracted with hot water, and the small amount of manganese oxide remaining is filtered through a small filter. The two precipitates are then ignited together at a strong red heat, keeping the crucible lid partly open to admit air, until the weight is constant. The residue is Mn_3O_4.

B. **By precipitation as phosphate, $MnNH_4PO_4$, which is ignited and weighed as pyrophosphate.** Weigh about 0·5 g. of manganous sulphate or of potassium permanganate, dissolve in about 150 c.c. of cold water, acidify with dilute sulphuric acid and reduce permanganate with SO_2 solution. Add about 20 g. of ammonium chloride, stir until this is dissolved, and add 10 c.c. of a cold saturated solution of microcosmic salt. Make the liquid slightly alkaline with ammonia, stir well, and heat to boiling, until the precipitate of manganese ammonium phosphate becomes crystalline. Allow to cool, filter through a Gooch filter, wash with very dilute ammonia to remove all trace of chloride, dry and ignite inside another crucible. Weigh as pyrophosphate, $Mn_2P_2O_7$.

C. **By precipitation as anhydrous sulphide, MnS, which is ignited and weighed.** This method is also an accurate one, and is

carried out exactly as described for the estimation of zinc as sulphide (498, B). See also par. 531.

ESTIMATION OF MOLYBDENUM

517. A. By precipitation as mercurous molybdate, Hg_2MoO_4, and ignition of this to MoO_3. Weigh about 0·5 g. ammonium or other molybdate, dissolve in 70–80 c.c. of water, add a little ammonium acetate, and a slight excess of mercurous nitrate solution. Heat the liquid to boiling, allow the precipitate to settle, and test the clear liquid with more mercurous nitrate solution. Filter through a Gooch or glass filter, wash with water containing mercurous nitrate, dry and heat carefully to 500–600°. The residue is MoO_3.

B. **By precipitation as lead molybdate, $PbMoO_4$, which is weighed.** Prepare a solution of ammonium molybdate as in A; add 10 c.c. of dilute acetic acid and 5 g. of ammonium acetate dissolved in a little water. Heat the solution to boiling, precipitate the molybdate by gradual addition of lead acetate solution, and boil gently for half an hour. Filter through a Gooch or glass filter, wash with hot water. Dry at 150–200° and weigh the $PbMoO_4$.

This method is useful as a magnifier for the determination of small quantities of phosphoric acid in minerals or of phosphorus in alloys, which dissolves as H_3PO_4. This is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4 . 12MoO_3$, which is filtered, washed and dissolved in NH_4OH. Ammonium chloride and acetate are added, the solution heated to boiling and the molybdate precipitated by adding a hot mixture of lead acetate and enough conc. HCl to keep the $PbCl_2$ in solution. The $PbMoO_4$ is treated as above. Each atom of phosphorus is equivalent to $12PbMoO_4$, so that the phosphorus present = $PbMoO_4 \times 0{\cdot}00704$.

ESTIMATION OF TUNGSTEN

518. By precipitation as benzidine tungstate and ignition of this to WO_3, which is weighed. Prepare the benzidine solution by dissolving 10 g. of benzidine in water with the addition of 15 c.c.

of concentrated HCl. Warm until dissolved, filter if necessary and make up to 500 c.c.

Weigh 0·4–0·5 g. of sodium tungstate, $Na_2WO_4 . 2H_2O$, dissolve in 150–200 c.c. of water and add about 10 c.c. of 0·1N. sulphuric acid. Heat to boiling and add 40 c.c. of the benzidine solution. The tungsten is completely precipitated as benzidine tungstate, together with some benzidine sulphate, which is very sparingly soluble. The mixed precipitate is more easily filtered than the pure tungstate. Allow the liquid to cool, filter and wash with a cold mixture of 10 c.c. of benzidine reagent in 250 c.c. of water. After ignition the residue is WO_3.

ESTIMATION OF TITANIUM

519. By precipitation with cupferron, and ignition to TiO_2, which is weighed. Cupferron is the trivial name for ammonium nitroso-phenyl-hydroxylamine, which precipitates iron (ferric), titanium and zirconium completely in strongly acid solutions.

Titanium in minerals may be estimated by fusing the fine powder with sodium pyrosulphate and dissolving the melt in dilute sulphuric acid. Filter and again fuse the residue with pyrosulphate, dissolve in dilute H_2SO_4, and filter from any SiO_2 and $BaSO_4$. To the united filtrates add 5 g. of tartaric acid and excess of ammonia, and precipitate the iron with H_2S. Acidify the filtrate with H_2SO_4 and boil off H_2S. To the cool solution add a 6 per cent. aqueous solution of cupferron, stirring meanwhile, until the reagent is in excess. Filter, wash with a 1 per cent. solution of the reagent, dry and ignite to TiO_2.

ESTIMATION OF SODIUM

520. By conversion into anhydrous sulphate, which is weighed. Compounds of sodium with volatile or organic acids are readily decomposed by heating with a little concentrated sulphuric acid, forming sodium sulphate.

Place 0·5 g. of sodium chloride in a weighed platinum crucible, add two drops of sulphuric acid and cover with the lid. When the reaction subsides, warm gently until no more HCl is evolved.

Allow to cool, add two more drops of sulphuric acid and heat, gently at first and afterwards to dull redness, until all free acid is expelled. Repeat this treatment till the weight is constant. The residue is Na_2SO_4.

This method applies also to the corresponding compounds of metals whose sulphates are not decomposed on heating, e.g. potassium, barium, lead, etc. See Molecular Weights, **31.**

ESTIMATION OF POTASSIUM

521. A. **The method given above** for sodium may also be employed for potassium, in its compounds with volatile or decomposable acids.

B. **By precipitation as potassium platinichloride, K_2PtCl_6, which is weighed.** In a porcelain dish place 0·3–0·4 g. of potassium chloride, dissolve in a little water, add a few drops of dilute HCl, and excess of platinum chloride solution. The double salt separates slowly, but is slightly soluble in water. Evaporate, therefore, to dryness, allow to cool, and extract with 50–60 c.c. alcohol. If this does not become yellow in colour, more platinum chloride must be added, and the evaporation and extraction with alcohol repeated. Filter the heavy, yellow precipitate through a weighed filter, wash with alcohol, dry at 100° and weigh. The residue is K_2PtCl_6.

Instead of weighing the potassium platinichloride on a tared filter, it may be filtered, dried, and ignited in a porcelain crucible, when a residue of metallic platinum and potassium chloride, $Pt + 2KCl$, is obtained.

This method serves for the separation of potassium from sodium, the platinichloride of the latter being soluble in water or alcohol.

C. **By conversion into perchlorate, $KClO_4$, which is weighed.** Weigh out some potassium chloride as above into a porcelain dish, dissolve in a little water and add an excess of perchloric acid, above 50 per cent. more than the theoretical quantity. Evaporate to a syrup on the steam, and then heat carefully over a small flame until white fumes of perchloric acid begin to appear. Allow to cool, add a little water to redissolve the salts, and again evaporate to complete the conversion of chloride into perchlorate.

When the residue is almost dry, allow to cool, and mix it with 13–20 c.c. of alcohol containing 0·2 per cent. of perchloric acid. Allow to stand for a short time and decant the liquid through a Gooch filter. Repeat the decantation with alcohol, wash the residue of $KClO_4$ into the filter with more alcohol, dry at 130–140° and weigh the $KClO_4$.

This method also serves for the separation of potassium from sodium, the sodium perchlorate being soluble.

D. **By precipitation with sodium cobaltinitrite.** This method does not give complete separation of potassium from sodium, but the precipitate in dilute acetic acid solution has the composition $K_2Na[Co(NO_2)_6]$. The potassium solution should be reduced to a small volume, cooled, excess of the reagent (187) added, the mixture allowed to stand overnight. It is then filtered through a Gooch crucible, washed with dilute acetic acid, then with alcohol, dried at 110° and weighed. The precipitate contains 17·927 per cent. of potassium.

Alternatively, the moist precipitate may be treated for the estimation of nitrite volumetrically (443), or the cobalt may be determined electrolytically (547).

ESTIMATION OF AMMONIUM

522. A. **By precipitation as ammonium platinichloride, $(NH_4)_2PtCl_6$.** The procedure is exactly that described above for potassium, and the precipitate may either be collected on a weighed filter and weighed as such, or ignited in the porcelain crucible, when metallic platinum alone remains.

B. **Ammonium is usually determined** by distillation of the ammonium compound with excess of caustic alkali, the liberated ammonia being collected in an excess of acid, and determined either as platinichloride, or volumetrically. For the latter method see par. 424.

ESTIMATION OF NITRIC ACID

523. A. **By reduction to ammonia.** If the nitric acid is free, it must be neutralised with sodium or potassium hydroxide, and the resulting solution used.

Weigh out about 1 g. of potassium nitrate into the flask of the ammonia distillation apparatus (Fig. 74, par. 424), and carry out the reduction as in **425.** Other reducing agents such as a zinc-copper couple or aluminium amalgam may be used. Proceed as in par. 425.

B. **By ignition of the nitrate with silica, when nitric anhydride is expelled.** Powder some quartz, or purify some fine sand by digesting with concentrated HCl, washing and drying. Place several grams in a platinum crucible, and ignite until the weight is constant. Now place about 0·5 g. of the dried nitrate in the crucible, mix it with the quartz by means of a platinum wire, and weigh again. Heat gently for about half an hour, cool and weigh, and repeat till the weight is constant. The loss in weight is the nitrogen pentoxide, N_2O_5.

C. **By precipitation with nitron.** This is a complex monacid organic base of the composition $C_{20}H_{16}N_4$, which forms an insoluble nitrate. It is used in 10 per cent. solution in N. acetic acid. Weigh 0·1–0·2 g. of the nitrate, dissolve in about 100 c.c. of water, acidify with acetic acid and add to the hot solution 10–12 c.c. of the nitron acetate solution. Let the precipitate settle in the ice-chest, or surrounded by ice-water, for several hours. Filter, wash with ice-water saturated with nitron nitrate, and dry at 110°. The precipitate contains 16·787 per cent. of HNO_3.

For the gas-volumetric method, see par. **556.**

ESTIMATION OF CARBONIC ACID

524. A. **By decomposing the carbonate and finding the loss in weight due to the escape of carbon dioxide.** The decomposition may be effected either by ignition (in some cases only) or by treatment with acids.

Carbonates of copper, nickel, zinc, magnesium, etc., are readily decomposed on ignition, leaving an oxide of known composition. The carbonate should be dried at 110° before use.

All carbonates are decomposed by treatment with hydrochloric acid. The experiment may be carried out in the Schrötter

apparatus (Fig. 80). In this, which is made entirely of glass, the hydrochloric acid (equal parts of conc. acid and water) is contained in the tube *a*, while the escaping carbon dioxide is dried by being caused to pass through sulphuric acid in the tube *b*. The apparatus is charged with these acids and weighed; about one gram of the carbonate is then placed in the flask, and the whole again weighed. The hydrochloric acid is slowly run into the flask so that the carbon dioxide is expelled at the rate of 3–4 bubbles per second. The flask is then gently warmed on a sand-bath, while a current of air is slowly drawn through the liquid by attaching an aspirator to the upper end of *b*. In this manner the carbon dioxide may be completely removed from the apparatus, which is then allowed to cool and weighed. The loss of weight represents the carbon dioxide.

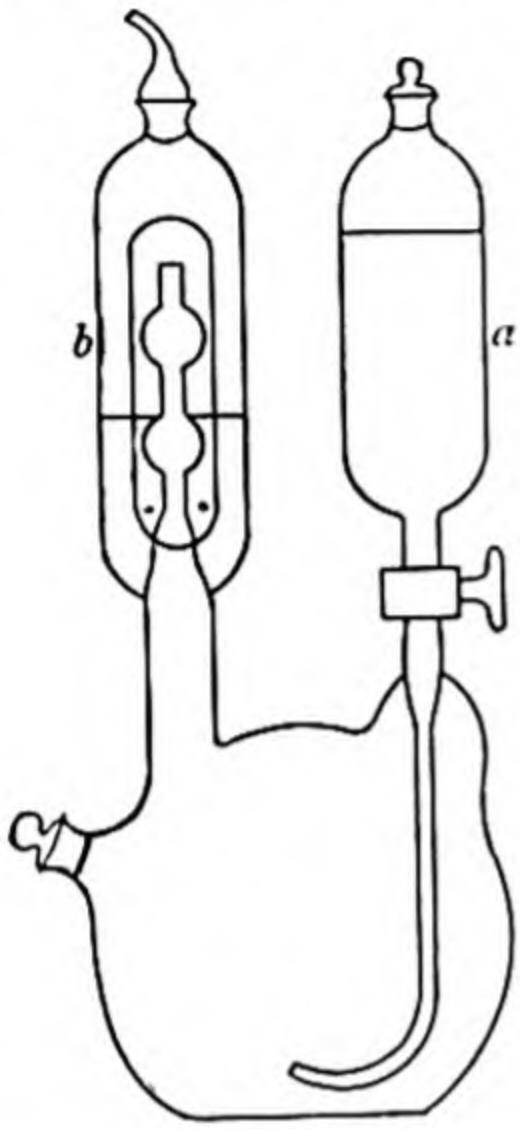


FIG. 80.

B. **By decomposing the carbonate and absorbing the carbon dioxide, which is then weighed.** The apparatus shown in Fig. 81

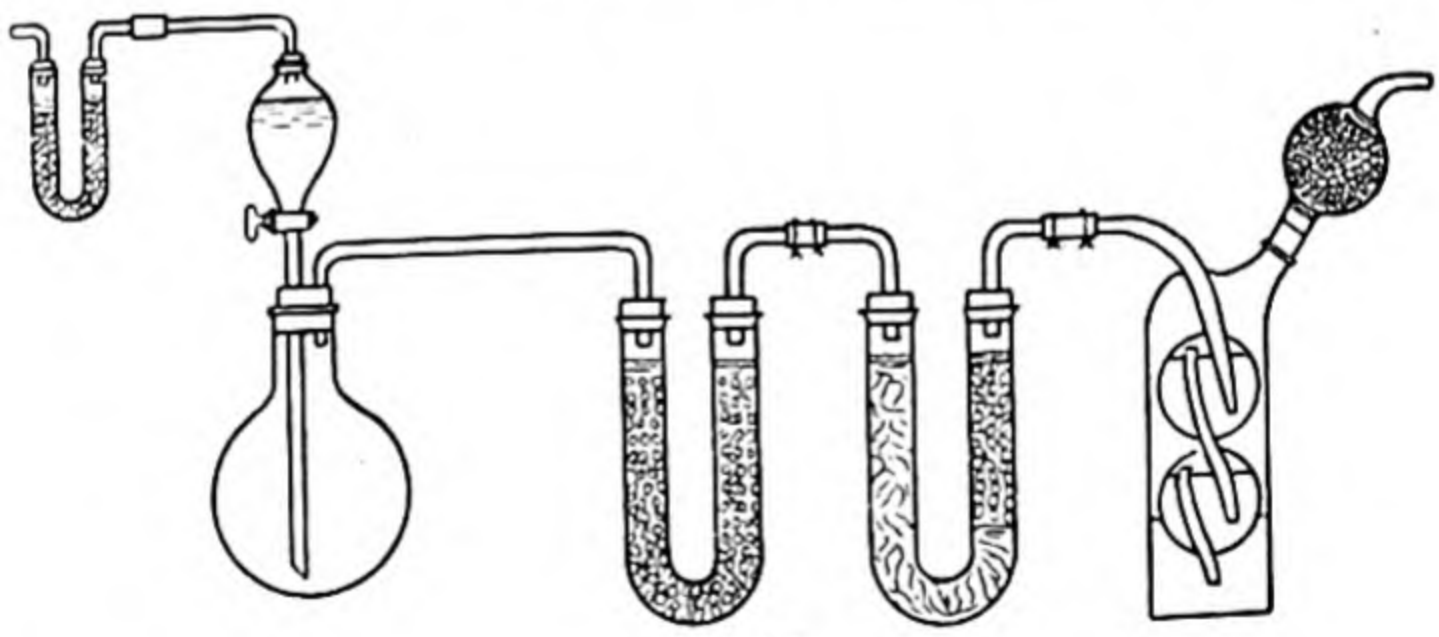


FIG. 81.

may be employed for this method, which is a very accurate one. The weighed carbonate is contained in the round flask (100 c.c.), which is fitted with a rubber stopper carrying a tap-funnel reaching to the bottom of the flask, and a delivery tube. The latter

should be of one piece of glass, and connects the flask with the first U-tube. This is filled with anhydrous calcium chloride, to dry the gas. The second U-tube is filled for the first two-thirds of its length with small fragments of pumice impregnated with anhydrous copper sulphate (by soaking in strong copper sulphate solution and gently igniting the drained material), which removes hydrochloric acid from the gas. The remainder of the tube is filled with calcium chloride to retain traces of moisture from the copper salt, the two materials being separated by a plug of glass wool. The gas is then absorbed in the potash bulbs, which contain a solution of caustic potash (1 part) in water (2 parts).

The potash tube is carefully weighed, and connected to the U-tube by a short piece of tightly fitting rubber tube. The glass tubes should be in contact, and the rubber fastened on each by a single turn of thin copper wire. A little water is added to the carbonate in the flask, and hydrochloric acid is then slowly added from the funnel, until all the carbonate is decomposed. The flask is then gently warmed, and air slowly aspirated through the apparatus until 5–6 times the volume of the latter has been passed. The air thus drawn into the apparatus is first freed from carbon dioxide in the small soda-lime tube attached to the top of the funnel. The potash tube is then detached and the ends are at once closed by means of rubber caps. It is allowed to cool in the balance-room for half an hour, and weighed, first removing the rubber caps.

Note.—In weighing comparatively large glass vessels such as these, the weight will be found to increase slightly during the operation of weighing, owing to slow condensation of moisture on the surface of the glass. The apparatus should be wiped carefully with a silk cloth immediately before weighing, taking care not to warm it by contact with the hands. Then weigh always at the same speed, and correct differences of weight will be obtained.

ESTIMATION OF SULPHUR IN SULPHIDES

525. A. By oxidation to sulphuric acid, and conversion of this into barium sulphate, which is weighed.

1. Place 0·5 g. of finely powdered zinc blende or copper pyrites in a nickel crucible containing a mixture of 3 g. potassium nitrate with 4 g. anhydrous sodium carbonate, or 3–4 g. of sodium peroxide with 2–3 g. carbonate. Mix by means of a platinum wire or glass rod, heat the covered crucible, gently at first, and finally until the contents are completely fused. When cool, extract with hot water, filter, acidify with hydrochloric acid, and proceed as in the determination of sulphuric acid (492).

2. **The oxidation** may also be effected by fuming nitric acid. Weigh the sulphide into a flask, place a filter funnel in the neck, and through this add some of the acid. When the first violent reaction is over, warm the flask gently until the oxidation is complete, and any free sulphur dissolved. Rinse the funnel, dilute with water, filter and determine the sulphuric acid as usual.

3. **Solutions** of sulphuretted hydrogen, or of alkaline sulphides, may be oxidised with bromine water. This is added in excess, the liquid warmed for half an hour, then boiled to expel the free bromine, and the sulphuric acid determined with barium chloride.

B. **A volumetric method** of determining sulphuretted hydrogen by means of standard iodine is described in par. **461.**

ESTIMATION OF SULPHUR IN COAL

526. Eschka's method, applicable to most non-volatile sulphur compounds, is to heat the substance with a mixture of sodium carbonate and twice its weight of magnesium oxide. The sulphur is completely converted into sulphates of soda and magnesia.

Take 1 g. of finely powdered coal and mix well with 3 g. of the Eschka mixture on glazed paper. Place the whole in a silica tray or crucible, and cover with a little more of the Eschka mixture. Begin heating gently to drive off the volatile matter, and when this has gone increase the temperature to a full red heat, until all the carbon is oxidised.

When cold, wash the residue into a beaker and boil gently to dissolve the sulphates (and possibly sulphites). Filter and wash the insoluble residue with hot water. To the filtrate add 20–25 c.c. of bromine water and heat gently for 10–15 minutes. Acidify

with HCl, boil off the excess of bromine, and estimate the sulphate as $BaSO_4$.

ESTIMATION OF SULPHUROUS ACID

527. A. **By oxidation to sulphuric acid.** The oxidation may be effected with bromine water, boiling off the excess; or with chlorine water, or hydrogen peroxide or materials that generate it. Hydrogen peroxide solution must always be tested for sulphuric acid, and a correction made for this if present.

When the oxidation is complete, the sulphuric acid is estimated as $BaSO_4$.

Since sulphurous acid and commercial sulphites are liable to contain sulphate, a separate estimation of this should be made.

B. **A volumetric method** for the estimation of SO_3'' is given in par. 459.

ESTIMATION OF THIOCYANIC ACID

528. A. **By oxidation to sulphuric acid.** This is the simplest method when no other sulphur compound is present. To the alkali thiocyanate solution add an excess of bromine water, and heat for about an hour on the steam pan. Acidify with hydrochloric acid and estimate the sulphate as $BaSO_4$.

B. **By precipitation with silver nitrate.** In the absence of halogen acids and HCN, add to the thiocyanate solution an excess of silver nitrate, acidify with HNO_3, and keep the mixture warm for half an hour. Filter through a Gooch crucible, dry at 120–130°, and weigh as AgSCN.

The volumetric method is described in par. 472.

C. **By precipitation as cuprous thiocyanate, $Cu_2(SCN)_2$.** In presence of sulphurous acid, copper sulphate solution precipitates the thiocyanate as cuprous salt. The method is similar to that used in the volumetric process (474), except that copper sulphate is added in excess, until the solution has a pale green colour, and the precipitate, after standing in the cold for 2–3 hours, is filtered through a Gooch crucible, washed with dilute H_2SO_3 solution, then with alcohol, and dried at 120–130°.

ESTIMATION OF HALOGEN OXYACIDS

529. Chloric acid is easily reduced to chloride by means of ferrous sulphate or zinc dust.

Take 0·3 g. of potassium chlorate, dissolve in water and add a solution of 5 g. of ferrous sulphate. Heat to boiling, stirring continually, and boil gently for half an hour. Alternatively, acidify the chlorate solution with acetic acid, add zinc dust and keep the liquid in this condition boiling for an hour. Then add nitric acid, and warm until the basic ferric salt, or the excess of zinc, is dissolved, filter if necessary and precipitate the chloride as AgCl (495).

The ignition method for chlorate is not a good one, as traces of chlorine are lost. For similar reasons bromate and iodate cannot be ignited.

Chlorate may, however, be decomposed quantitatively into chloride by ignition with 3–4 times its weight of pure NH_4Cl, until all ammonium salts are expelled and the weight is constant. Yet another method is to evaporate a mixture of the chlorate with repeated small quantities of dilute HCl, until the dry residue is pure chloride, of constant weight. These methods must be carried out in covered crucibles.

Iodic acid and **bromic acid** are best reduced by means of sulphurous acid, added in excess to a solution of the alkali iodate or bromate acidified with sulphuric acid. Then add an excess of silver nitrate followed by HNO_3, heat to coagulate the precipitated silver halide, and treat as described in par. **495.**

SEPARATIONS

ANALYSIS OF A SILVER ALLOY

530. Weigh accurately about 0·8 g. of a silver alloy (coin), place in a porcelain dish, cover with a clock-glass, and add a little water and concentrated nitric acid. When the metal is dissolved, rinse the clock-glass, and evaporate to expel most of the acid.

Add water, transfer to a beaker, and precipitate the silver as chloride. Filter, wash only on the filter and not by decantation,

adding the first two washings to the filtrate. Complete the washing and further treatment of the precipitate as described for the estimation of silver (495).

The copper in the filtrate may be estimated as sulphide (491, B) or thiocyanate. For the latter, the liquid must not contain free nitric acid. Neutralise this by adding ammonium hydroxide until a slight precipitate is produced, then add some freshly prepared sulphurous acid, and excess of ammonium thiocyanate. The copper is completely precipitated as white cuprous thiocyanate, $Cu_2(SCN)_2$. Filter through a weighed Gooch or fritted glass filter, dry at 100° and weigh, or convert to cuprous sulphide. Nickel, if present, may then be estimated in the filtrate as hydroxide or dimethylglyoxime salt (502, B).

SEPARATION OF IRON AND MANGANESE

531. When these two metals occur together, as in minerals, the precipitation of iron as ferric hydroxide always brings down some of the manganese. To effect the separation of the metals, the iron (and aluminium, if present) is first precipitated as basic ferric acetate, the manganese being left in solution and determined in the filtrate.

For practice in the method, weigh accurately about 1 g. of ferrous ammonium sulphate and 0·8 g. of manganous sulphate into a 500 c.c. beaker, dissolve, and oxidise the iron by boiling with nitric acid. Add ammonium carbonate solution gradually, keeping the beaker covered, until a very slight precipitate remains undissolved. The liquid is now deep reddish brown in colour. Now add a little acetic acid to redissolve this precipitate, and then a solution of 3–4 g. of ammonium acetate in 10–15 c.c. water. Boil gently until the liquid is perfectly colourless (203, 3). The ammonium acetate represses the ionisation of the acetic acid, so that the *p*H value of the solution remains practically constant (see Buffer solutions, 408).

Filter the liquid as quickly as possible, transfer the precipitate to the filter, and wash twice with boiling water. To remove a small quantity of manganese which may be contained in the precipitate, redissolve the latter in hydrochloric acid, and repre-

cipitate the iron from this solution exactly as described above. Filter at once and wash the precipitate on the filter with boiling water, adding the first three washings to the filtrate. Combine the two filtrates and estimate the manganese as described below. The precipitate may be again redissolved in hydrochloric acid and the iron precipitated by ammonia, or it may be ignited at once, when ferric oxide remains.

To estimate the manganese, the carbonate or sulphide method (516) may be employed, but it is better, for the separation of manganese in mineral analysis, to proceed as follows. Add bromine water to the filtrate until it has a strong yellow colour, then add excess of ammonia, warm the liquid and allow to stand overnight in a warm place. Filter, test the filtrate with more bromine water and ammonia, wash and ignite the precipitate. The residue is Mn_3O_4.

SEPARATION OF IRON AND ALUMINIUM

532. These metals are precipitated together as hydroxides or basic acetates, and there is no reliable gravimetric method of separating them, although potassium hydroxide is often employed for this purpose.

Weigh out about 1 g. each of iron alum and potash alum and dissolve in a little water. If an acid solution is being examined, it should be nearly neutralised. Pour the neutral or slightly acid solution into 50 c.c. of a strong solution of potassium hydroxide, which is kept just boiling, with constant stirring, in a platinum or silver dish. Ferric hydroxide is precipitated, and is filtered and washed, redissolved in hydrochloric acid and reprecipitated by ammonia, to free it from potash. The aluminium is determined in the filtrate by neutralising with hydrochloric acid and then precipitating with ammonia.

The most accurate method, however, is as follows. Make up the solution to 250 c.c. with distilled water ; of this solution take 100 c.c. and determine the iron and aluminium together by precipitating with ammonia (499).

Then estimate the iron in the original solution by reducing portions of 25 c.c. and titrating with standard dichromate (445).

From the weight of iron found, calculate that of Fe_2O_3 in the combined $Fe_2O_3 + Al_2O_3$ precipitate, and thus find the weight of alumina.

8-Hydroxyquinoline has been suggested* as a means of separating iron from aluminium if the *p*H value of the solution does not exceed 3·5–4. But at *p*H 4·1 co-precipitation of aluminium sets in by adsorption on the iron 8-hydroxyquinoline salt, and increases with the *p*H value in accordance with Freundlich's adsorption equation.

ANALYSIS OF DOLOMITE

533. In this and all other complex analyses it is necessary first to make a complete qualitative analysis, and then to prepare a scheme for the separation and estimation of the constituents which have been found. In the case of dolomite and other limestones, it will be necessary in general to estimate the insoluble matter, iron, aluminium, manganese, calcium and magnesium, and also carbonic acid and moisture. Grind about 10 g. of the sample to fine powder, and place it in a weighing bottle.

Estimation of insoluble matter. Weigh about 2 g. of the powder into a porcelain dish, cover with a clock-glass and add hydrochloric acid little by little until the effervescence ceases. Add some more hydrochloric acid, a little nitric acid, and evaporate on the water-bath to complete dryness. Heat the residue with a little concentrated hydrochloric acid to dissolve all the soluble portion, add hot water, filter and wash, dry and ignite the insoluble matter. This consists mainly of silica and clay.

Estimation of iron and aluminium. If manganese is absent, the iron and aluminium hydroxides may be precipitated with ammonium chloride and ammonia, filtered, redissolved in hydrochloric acid, and reprecipitated with ammonia, to remove traces of calcium adsorbed in the first precipitate. The ignited residue of iron and aluminium oxides, after weighing, is dissolved by digesting for a long time with concentrated hydrochloric acid, the iron reduced with zinc or sulphurous acid and estimated with dichromate.

* Moger and Remington, *Ind. Eng. Chem.* (*Anal.*) **10**, 212 (1938).

Estimation of manganese. If manganese is present, the iron and aluminium are precipitated as acetates, as described in par. 531, and the manganese determined by precipitation as hydrated peroxide, and ignition to Mn_3O_4.

Estimation of calcium. The filtrates and washings from the iron, aluminium and manganese precipitates are combined, and evaporated if necessary. If there is much lime in the mineral, take one half of the liquid, make alkaline with ammonia, and precipitate the calcium as oxalate, by adding excess of ammonium oxalate to the boiling liquid. Filter, wash two or three times, and redissolve the precipitate in hydrochloric acid. Again precipitate with ammonium oxalate, and estimate the calcium as oxide, as described in par. 504. This solution and reprecipitation of the calcium oxalate removes traces of magnesium which may be adsorbed in the first precipitate (101).

Estimation of magnesium. Evaporate the filtrates and washings from the calcium precipitates to dryness in a 6-inch porcelain dish, and ignite on a sand-bath until nearly all ammonium salts are expelled. These, when present in excess, prevent the complete precipitation of magnesium.

To the residue add a little hydrochloric acid, heat on the steam-bath, add hot water, and filter if necessary. Make the solution alkaline with ammonia, and precipitate the magnesium as magnesium ammonium phosphate. Treat this as described in par. 508.

Estimation of carbon dioxide. Weigh accurately 1·5–2 g. of the powdered mineral into the flask of the carbon dioxide apparatus (524), and determine the carbon dioxide exactly as described.

The potash tube should be recharged when about half the quantity of carbon dioxide corresponding with the amount of potash it contains has been absorbed. This can be ascertained from the increase in weight in successive estimations.

Estimation of moisture. Weigh about 2 g. of the powder in a watch-glass, which is covered by a second watch-glass, the two being held together by a brass wire clip. Remove the upper glass and heat the powder for an hour in the air-oven at 200°.

Allow to cool in the desiccator, after replacing the cover glass and clip. Repeat the heating until the weight is constant. The loss in weight is due to the moisture.

INDIRECT ESTIMATION OF ALKALIS IN ROCHELLE SALT

534. The metals sodium and potassium are contained in Rochelle salt in equivalent quantities, and in many other compounds, such as glass, felspars, etc., they occur in varying proportions. In both cases they may be estimated, without separating the potassium as potassium platinichloride (**521**, B), by the following method.

Weigh about 2 g. of Rochelle salt into a platinum crucible, and heat gently until the water of crystallisation is expelled and the salt begins to char. Increase the temperature gradually until the crucible is at a dull red heat. The salt is now completely decomposed, and the metals remain as carbonates.

Extract with hot water, filter off the carbon and wash thoroughly with hot water. Acidify the solution with hydrochloric acid, and evaporate to dryness in a platinum dish on the water-bath. Dissolve in water and again evaporate to dryness, to expel free hydrochloric acid, and then heat the residue to 150° in the air-bath until the weight is constant. This gives the weight of mixed chlorides.

Again dissolve in water, and determine the chlorine by titration with silver nitrate (**464**), or gravimetrically (**495**).

The amounts of sodium and potassium may now be calculated. Let A = weight of chlorides, B = weight of silver chloride, x = weight of sodium chloride and $(A - x)$ = weight of potassium chloride. Then we have

$$x\frac{143{\cdot}5}{58{\cdot}5} + (A - x)\frac{143{\cdot}5}{74{\cdot}5} = B,$$

from which x and $(A - x)$ may be found, and from these, the weights of sodium and potassium.

The indirect method may also be applied to the determination of mixtures of carbonates by estimating the carbon dioxide, mixtures of sulphates, and many others.

FELSPAR AND OTHER INSOLUBLE SILICATES

535. The felspars are essential constituents of crystalline igneous rocks, and are all silicates of alumina with potash, soda or lime in varying proportions. Owing to alteration, they usually contain small quantities also of iron and magnesium. Orthoclase is the monoclinic felspar, a potash alumina silicate of the composition $KAlSi_3O_8$, which occurs in such rocks as granite and syenite. In addition to the constituents indicated in the formula, it always contains some iron, lime, magnesia and soda, while in other silicates, manganese, also, is nearly always present. The mineral must be very finely powdered, first in the percussion mortar (par. 5) and then in the agate mortar.

Estimation of silica. Fusion with sodium carbonate or fusion mixture. Weigh accurately 1–1·5 g. of the finely powdered mineral into a platinum crucible, and add 5–6 times this weight of fusion mixture. (See note on the use and care of platinum vessels, par. 490.) Stir carefully with a thin glass rod or a stout platinum wire, and when the materials are thoroughly mixed, rinse the rod or wire with a little more of the carbonate. The crucible should not be more than half full. Heat gently at first, until most of the carbon dioxide has escaped, and then more strongly until the mass is completely fused, and the reaction is judged to be complete. When cool, place the crucible in a porcelain dish, add a little hot water, and warm over the steam until the mass can be detached from the crucible and the latter rinsed and removed. Now cover the porcelain dish with a clock-glass, and carefully acidify the liquid by adding concentrated hydrochloric acid in small quantities. Rinse and remove the clock-glass, and evaporate the liquid to dryness. The gelatinous silicic acid which separates should be broken up frequently by stirring with a glass rod. In order to remove the hydrochloric acid more completely, the residue in the dish should be moistened with water and again evaporated; and to ensure complete drying, and also to render the silica less soluble, the dish and residue are then heated in the air-bath for an hour at 130–140°. When cold, the residue is moistened with moderately concentrated hydro-

chloric acid, allowed to stand for half an hour, diluted with warm water, and heated on the steam-bath. The insoluble silica is then filtered, washing by decantation with warm water, and again on the filter until quite free from chlorides. The silica may be at once transferred to a weighed platinum crucible, without drying, care being taken to wrap the upper edge of the paper over the moist silica, and the whole ignited, gently until dry, and then strongly until the weight is constant.

The filtrate usually contains a little silica, which may be removed by evaporating to dryness and repeating the above process. For most purposes, however, this is unnecessary.

Estimation of the heavy metals. The filtrate contains the iron, aluminium, calcium, magnesium and alkalis. Lead, if present, is precipitated with H_2S (506, C). After filtering, if necessary, the filtrate is boiled with a little nitric acid to oxidise iron, which is then precipitated together with alumina by adding a slight excess of ammonia and boiling. The iron and aluminium may be separated as in par. 532 or 533. If manganese is present, the characteristic bluish-green colour usually appears during the fusion for silica. In this case separate the manganese by the method given in par. 531. If barium be present, it is estimated as sulphate (494). Calcium and magnesium are then estimated as in the analysis of dolomite.

Estimation of alkalis. The alkali metals cannot be determined in the above analysis, since alkali carbonates are employed in the fusion, but they may be estimated by one of the following methods :

A. **Decomposition with ammonium chloride and calcium carbonate.** Weigh accurately about 1 g. of the mineral, which must be in the finest possible state of division, and mix well with an equal weight of pure ammonium chloride by grinding in an agate mortar. Then add 6 g. of pure calcium carbonate, mix well and transfer to a platinum crucible. It need scarcely be pointed out that the reagents used must be quite free from alkalis ; if there is any uncertainty, a blank experiment should be made, and if necessary the materials must be purified. The crucible is covered, heated gently for about ten minutes, and then for an hour with

the lower portion of the crucible at a red heat. The alkali metals are thus converted into chlorides. When cold, the crucible is placed in a porcelain dish and the mass extracted with hot water and filtered. The filtrate contains sodium and potassium chlorides, with some calcium and possibly magnesium chloride. A little ammonia, ammonium carbonate, and ammonium oxalate are added, the liquid boiled and filtered, and the filtrate evaporated to dryness. It may still contain a little calcium or magnesium, to remove which it is again dissolved in water, and the treatment with ammonia and ammonium oxalate repeated. The liquid is again evaporated to dryness, and the residue ignited to expel ammonium salts. A little carbonate may remain from the decomposition of the oxalate; to remove this, moisten with dilute HCl, and if magnesium be present it may be removed at this point by digesting for an hour or two with moist mercuric oxide. Filter, evaporate to dryness, and ignite to expel any mercuric chloride. Moisten with dilute HCl, transfer to a weighed platinum dish, filtering if necessary, and evaporate to dryness. Again add a little water and evaporate, to remove the last trace of acid. Finally heat in the air-bath at 150° until the weight is constant. From the mixed chlorides thus obtained the potassium may be precipitated as platinichloride or cobaltinitrite (521), and the sodium found by difference, or the metals may be determined by an indirect method (534).

B. **Decomposition with hydrofluoric acid.** Weigh about 1 g. of the finely powdered mineral into a platinum crucible, moisten with water and add 10 c.c. of pure hydrofluoric acid. Allow to stand in the fume-chamber for an hour, then warm gently and evaporate to dryness. The silica is removed as silicon fluoride, and the metals remain as fluorides. Now add dilute sulphuric acid, and evaporate in a platinum dish to remove hydrofluoric acid. As this is very poisonous, care must be taken not to inhale it. Dissolve the residue in water, and, without filtering, precipitate the sulphuric acid with excess of barium hydroxide, keeping the mixture hot on the steam-bath. Iron, alumina, manganese, etc., are also precipitated. Filter, and from the filtrate remove barium amd calcium with ammonium carbonate. If magnesium

is present it may be removed as described above, leaving the alkali chlorides.

Water may be determined by the method given for dolomite (533), or if no other volatile matter be present, by ignition in a weighed crucible. **Carbon dioxide,** if present, is determined in a separate portion of the mineral (524-5).

ANALYSIS OF GLASS

536. The methods given above for felspar (535) will serve, with little or no modification, for the analysis of all kinds of glass. Ordinary glass is mainly a mixture of silicates of lime and soda. Hard or " combustion " glass contains potash in place of a portion or the whole of the soda. Flint-glass, sometimes called crystal-glass or crystal, is a silicate of potash and lead. Common bottle-glass contains lime and alumina, together with the alkalis. Any kind of glass may be coloured by the use of certain metallic oxides, the colours obtained being similar to those seen in the borax bead or microcosmic bead. Opaque glass is made by the addition of cryolite, arsenious oxide, bone-ash, or fluor-spar.

The fusion is carried out as with felspar, and the subsequent treatment is similar, except that **lead** must be separated as sulphide (506, C) before the precipitation of iron, aluminium, etc. In presence of lead, owing to the difficulty of removing the sparingly soluble chloride of lead from the residue of silica, nitric acid may be used after the fusion instead of hydrochloric acid, and should then be removed from the filtrate before the precipitation of sulphides, by evaporating to dryness, and repeating the evaporation with hydrochloric acid.

When any uncertainty exists regarding the composition of the glass, a preliminary qualitative analysis should be made, and a scheme may then be devised for the quantitative examination.

SILICATES DECOMPOSED BY ACIDS

537. Silicates which are soluble in water (water-glass, etc.), and many that are insoluble, such as the zeolites and other hydrated mineral silicates, may be decomposed by treatment with

concentrated acids, and do not require fusion. If lead or silver be present, nitric acid may be used instead of hydrochloric acid.

Prehnite and natrolite may be taken as examples.

Estimation of silica. The finely powdered mineral should first be ignited, and the portion used for the determination of **water by ignition** may therefore be employed. Weigh about 2 g. in a platinum crucible, and determine the loss at a bright red heat over a Méker or Bray burner. This gives the total amount of water. Transfer the remainder to a porcelain dish, moisten with water, then cover with concentrated HCl, stirring frequently with a glass rod, and continue heating over the steam until the grittiness can no longer be detected by rubbing with the rod. Evaporate to dryness and proceed with the analysis as described in par. **535.**

The metals may be estimated in the filtrate as in the case of felspar.

ANALYSIS OF PYRITES, BLENDE, ETC.

538. Iron pyrites is essentially a sulphide of iron of the composition FeS_2, while copper pyrites is a copper-iron sulphide, $(CuFe)S_2$. Other metals also may be present, and it may be necessary to estimate arsenic, lead, nickel, cobalt, calcium, zinc; there is usually also some insoluble matter of a siliceous nature. Similar remarks apply to zinc blende, ZnS, galena, PbS, and other mineral sulphides. A qualitative analysis should always be made.

Estimation of sulphur. Use about 1–1·5 g., and determine the sulphur as described in par. **525,** by the use of fuming nitric acid, or acid of sp. gr. 1·4 with the addition of a little potassium chlorate from time to time. If any **insoluble matter** remains, filter and determine it as described in the case of dolomite **(533).** If **lead** is present (galena, etc.), either the insoluble matter should be washed on the filter with a warm solution of ammonium acetate, which dissolves $PbSO_4$, or the liquid evaporated to dryness with concentrated HCl, and extracted with HCl before transferring to the filter. To the filtrate, heated to boiling, add a hot solution of $BaCl_2$, and determine the sulphur as $BaSO_4$.

Saturate the filtrate with H_2S to precipitate **copper, lead, arsenic,** etc., and separate these by the methods used in qualitative analysis.

Copper and lead may also be determined in the filtrate, or in an aliquot portion of it, by the electrolytic method (**545**).

After removal of the sulphides, boil off H_2S, oxidise iron by boiling with HNO_3, and precipitate the **iron** with ammonia. If necessary, **aluminium** and **manganese** may be determined as in dolomite (**533**).

Precipitate **zinc** from the filtrate by saturating with H_2S, and determine the ZnS as in par. **498**, B.

The presence of barium chloride in the liquid makes it preferable to estimate **calcium** and **magnesium**, if present, in a fresh portion of the mineral. Dissolve as before, separate the other metals as just described, and determine the calcium and magnesium as in dolomite (**533**).

ANALYSIS OF BRASS, BRONZE, GERMAN SILVER, ETC.

539. Brass often contains small quantities of lead, tin and iron, while bronze, which is essentially an alloy of copper and tin, often contains also some zinc, lead, iron or other metals. A general method is therefore given for such alloys.

Weigh about 2 g. of the alloy (or more if small quantities of some metals have to be estimated), treat with HNO_3 (**512, A**), and when the action is over, evaporate almost to dryness. If tin is present it remains as metastannic acid. Moisten the residue with HCl, allow to stand for an hour or more, add water and allow the metastannic chloride to dissolve. From this solution precipitate the **tin** with NH_4NO_3 as described in par. **512**, B. To separate **lead**, evaporate almost to dryness with sulphuric acid; dilute with water, allow to stand, filter the $PbSO_4$, and estimate the lead as in par. **506**. The filtrate contains copper, zinc, with possibly iron, nickel or manganese. Make up to 500 c.c. Determine the **copper** in 100 c.c. by precipitation as sulphide (**491**, B), by the thiocyanate method (**530**), or by electrolysis (**545**). If the first method be employed, it is advisable to redissolve the precipitate of CuS in nitric acid, evaporate to dryness with HCl, and reprecipitate the CuS, in order to remove a small quantity

of zinc, or of nickel, which is usually adsorbed on the copper sulphide in the case of brass and German silver respectively.

If some of the remaining metals are present only in small amounts, it is advisable to remove the copper from a larger volume of the solution, by saturating with H_2S; or to make a determination of copper by two or more of the methods suggested above, and then combine the filtrates. In any case, mix the filtrates, and evaporate to dryness to expel H_2S. Dissolve the residue in a little water, transfer to a conical flask, nearly neutralise with KOH, add a little sodium acetate, and then saturate the warm solution with H_2S. Close the flask with a cork, and allow to stand overnight. Filter the ZnS and estimate the **zinc** as in par. 498, B. From the filtrate, **iron** and **manganese** (manganese bronze) may now be separated, after boiling off H_2S, by the method given in par. 531, and the filtrate from manganese will then contain **nickel**, which may be estimated as oxide or as metal (502), or by the method of electrolysis (547).

Aluminium bronze may be analysed by the above method, the aluminium being precipitated as hydroxide after removing copper, or separated from manganese by the acetate method (531), or as 8-hydroxyquinoline salt (500, B).

Phosphor bronze is the name given to alloys of copper and tin, containing some phosphorus. The metals may be determined as above, and the **phosphorus** is estimated by treating the metal with HNO_3 (512, A), or *aqua regia*, and evaporating to dryness. The residue, containing the tin as metastannic acid, together with phosphate of tin, is then dissolved by means of HCl and water (539). From this solution the phosphoric acid is precipitated by adding HNO_3 and excess of ammonium molybdate, and allowing to stand overnight in a warm place. The precipitate of ammonium phospho-molybdate is filtered, washed, dissolved in ammonium hydroxide, and the phosphoric acid precipitated as magnesium ammonium phosphate, which is then ignited and weighed as $Mg_2P_2O_7$.

ANALYSIS OF SOLDER, PEWTER, ETC.

540. Cut the solder into fine shavings, weigh out 0·5 g. into a 250 c.c. conical flask, and proceed as in par. 512, A, to estimate the

tin. The residue of SnO_2 is never pure, but contains some SbO_2 and PbO when these metals are present. A better method is given in par. 542.

To the filtrate add a slight excess of dilute sulphuric acid, and evaporate to dryness in a porcelain dish. Add 50 per cent. alcohol to the residue, allow to stand for an hour and filter. Wash the precipitate of $PbSO_4$ with 50 per cent. alcohol, and proceed from this point as in par. 506, A.

ANALYSIS OF TYPE METALS, BRITANNIA METAL, ETC.

541. Dissolve 1 g. of the alloy in *aqua regia*, add 10 g. of tartaric acid dissolved in a little hot water, and make the solution alkaline with pure sodium hydroxide. Pour into a basin containing 30 g. of sodium hydroxide in 500 c.c. of water, heat till gently boiling and pass sulphuretted hydrogen till saturated. Filter, wash with hot dilute sodium sulphide solution (prepared similarly to ammonium sulphide, par. 178), and then once with boiling water. The filtrate and washings are used for the estimation of tin and antimony.

Dissolve the precipitated sulphides (mainly PbS) in nitric acid, evaporate to expel the excess of acid, and filter from any trace of SnO_2, which must be preserved and added to the tin precipitate later. Evaporate the filtrate with sulphuric acid and estimate the lead as in 506, A. Precipitate the **copper** in the lead filtrate with H_2S and estimate as in 491, B. Precipitate **zinc** and **iron** with sodium carbonate, wash, dry, ignite and weigh as ZnO and Fe_2O_3 together. If present in sufficient quantity, the iron may be estimated separately in the lead filtrate, as in the separation from manganese (531).

To estimate the **antimony**, acidify the first filtrate with hydrochloric acid, warm and allow to stand to complete the precipitation of the sulphides. Filter and wash with H_2S water. Remove the precipitate from the filter paper by means of a silica or platinum spatula to a porcelain dish, dissolving any precipitate left on the paper in hot concentrated HCl. Add HCl to the contents of the dish, heat gently and add from time to time a crystal of $KClO_3$. Boil to expel chlorine, rinse the cover, filter into another

porcelain dish, and evaporate to a few c.c. Add a hot solution of 20 g. oxalic acid, transfer to a beaker, dilute with boiling water to 300 c.c. and pass H_2S until all the antimony is precipitated. Treat the precipitate as in 511, A.

To estimate the tin, add excess of HCl to the filtrate, heat and add solid $KMnO_4$ in small quantities until there is a slight precipitate of MnO_2. The oxalic acid is now destroyed. Redissolve the MnO_2 by adding a few drops of $FeSO_4$ solution, pour the liquid into a flask, and pass H_2S to precipitate the tin. Filter, wash with H_2S water containing a little ammonium nitrate. The precipitate contains SnS and S. Wash and dry. Remove the precipitate from the paper, burn the filter paper, place the ash in the crucible, add a few drops of HNO_3 and heat strongly. Now add the precipitate, and any SnO_2 obtained earlier, and heat in the open crucible to convert the sulphide to SnO_2. Continue heating until the weight is constant.

ANALYSIS OF SOLDER AND TYPE METAL (WHITE METALS)

542. The estimation of tin by HNO_3 is unsatisfactory, as the precipitate always contains SbO_2 and some PbO.

Tin is estimated preferably by titration with $FeCl_3$ solution. Proceed as follows : *

If the metal is completely soluble in HCl (e.g. solder) weigh 1 g. into a 400 c.c. flask, add 180–200 c.c. of pure conc. HCl, boil till dissolved and titrate *rapidly* at the boiling point with $FeCl_3$ solution. The best strength of solution is 1 c.c. = 0·02 g. of tin, and it should be standardised with *pure* $SnCl_2$, prepared by dissolving *pure* tin in hot concentrated HCl as in the estimation. One drop of the solution in excess gives a distinct yellow colour in *hot strong* solution.

If the metal is not completely soluble, weigh out 1 g., boil with 75 c.c. HCl till the action ceases, and add 5–10 g. of piano wire. This precipitates Sb, Cu, etc. Add thin strips of copper until a strip remains bright. All the Sb and As will now be precipitated. Add 40 c.c. hot boiled water, boil and filter rapidly

* L. Parry, *The Assay of Tin and Antimony.*

into another flask, washing out the flask and filter paper with hot dilute HCl. Keep from the air as much as possible. Precipitate the tin at once by adding strips of zinc until some remain undissolved. Test a portion of the liquid with H_2S. If the precipitate is white, no tin is present. Dilute and decant, as closely as possible, through a filter. Wash any particles back into the flask by making a hole in the filter and pouring through it 180 c.c. of concentrated HCl. Heat to boiling till all the tin is dissolved, and titrate the boiling solution rapidly with $FeCl_3$.

Antimony may also be estimated volumetrically.* Boil 1 g. with 100 c.c. HCl in a 500 c.c. flask until the action ceases. Add $KClO_3$ to dissolve the black powder of antimony. Dilute to nearly twice the bulk and boil off the chlorine. Cool, and when quite cold, fill the flask with CO_2, add 20 c.c. of a fresh 20 per cent. solution of KI and titrate as rapidly as possible with $SnCl_2$ (20 g. $SnCl_2 . 2H_2O$ in 300 c.c. HCl, made up to 1 litre. Keep the solution under CO_2 and standardise, every time it is used, against $K_2Cr_2O_7$, 16 g. per litre). Add starch paste near the end of the titration, and complete by adding $SnCl_2$ till the blue colour disappears.

ELECTROCHEMICAL ANALYSIS

543. The estimation of metals by electro-deposition can be easily carried out in nearly all cases, and is of very frequent application. According to Faraday's law, the weight of metal deposited from an electrolyte is proportional to the quantity of electricity which passes through the electrolyte, and is given by the relation that 1 gram-equivalent of any substance is deposited by 96,540 coulombs, that is, by a current of 1 ampere in 96,540 seconds, or 26 hours 49 mins. The electromotive force required depends upon the back E.M.F. of polarisation of the electrolyte, and since the use of this minimum E.M.F. would involve the expenditure of an infinitely long time in order to complete the deposition, in practice a current is used at 1 or 2 volts in excess of the polarisation E.M.F. In order to measure and to regulate

* L. Parry, *ibid.*

the current, an ammeter and a variable rheostat are included in the circuit, while a voltmeter is placed in a branch circuit. These

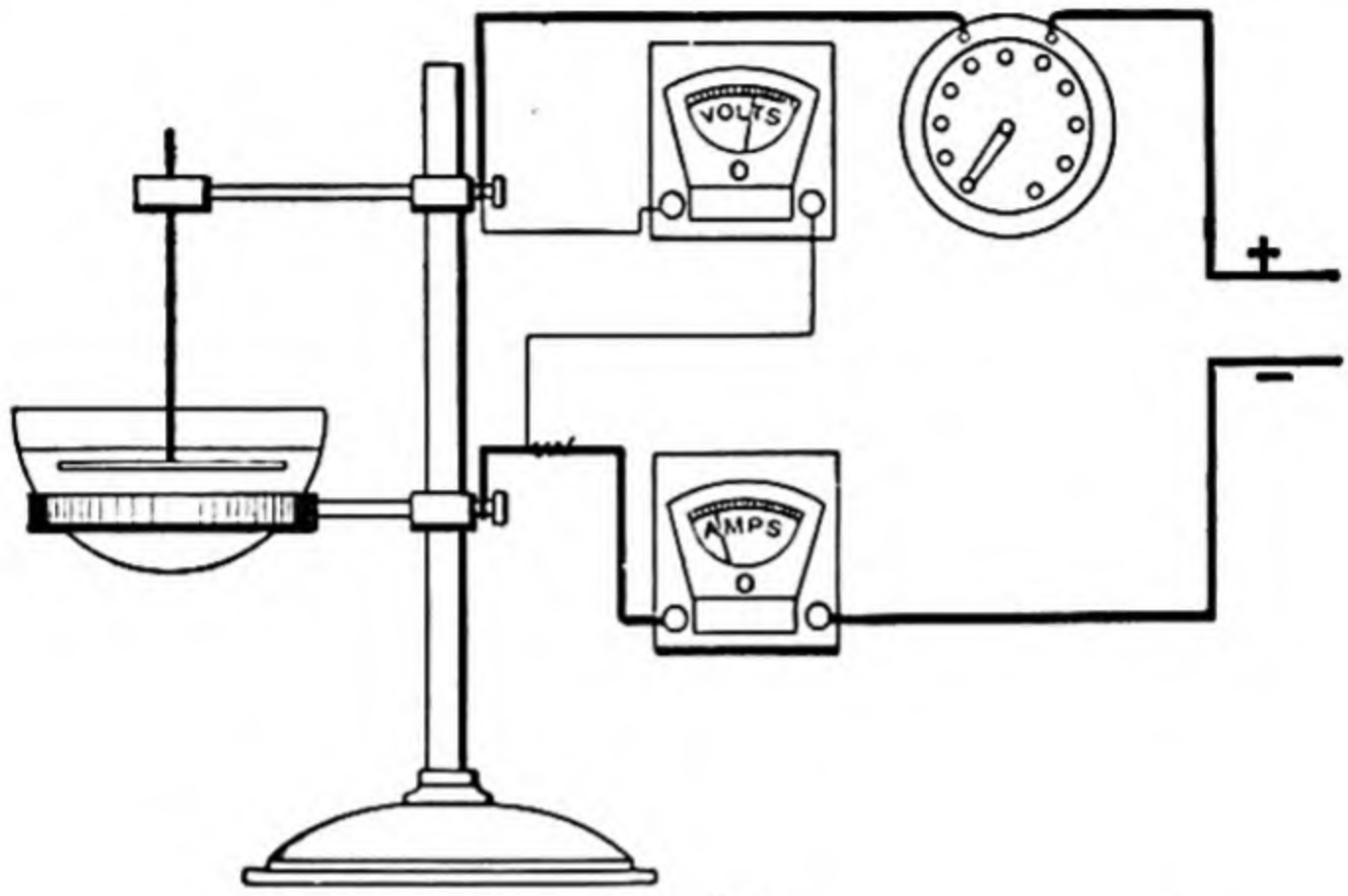


FIG. 82.

instruments should be fairly accurate, especially for experiments on the separation of one metal from a solution containing several. The current from a secondary battery of two or three cells is sufficient for most purposes.

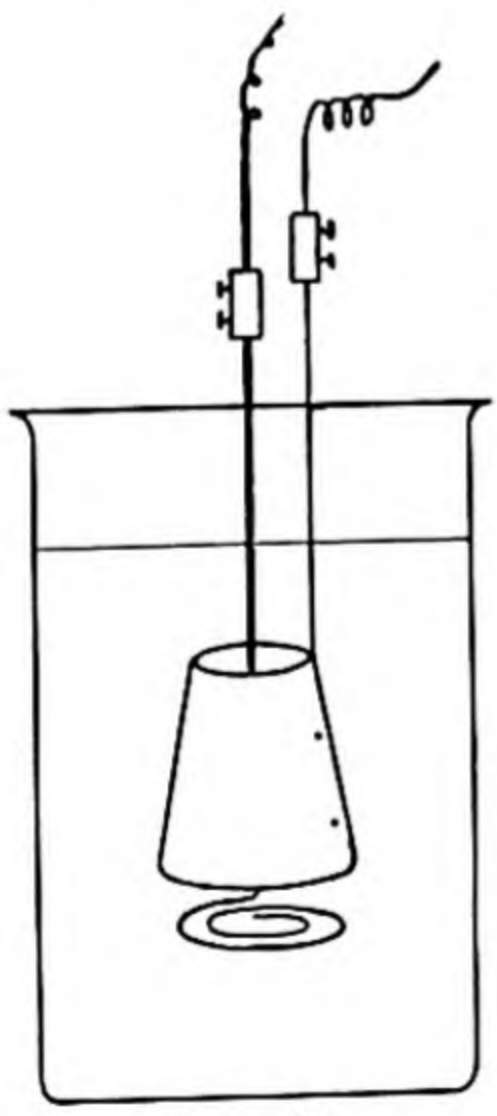


FIG. 83.

The general arrangement of the apparatus is shown in Fig. 82, which requires little explanation. The platinum dish forms the cathode, while the anode consists of a platinum disc, which may be perforated, or a flat spiral of stout platinum wire. As an alternative, the solution may be placed in a beaker, with the platinum cone (Fig. 83) as cathode, and the spiral anode. Many forms of electrodes are in use, the platinum dish being most commonly used as cathode. If the latter be roughened by sandblasting, the deposit will be more firmly adherent. The electrodes must, of course, be perfectly clean and free from any trace of grease, or good deposits cannot be obtained.

The time required for a deposition is generally much longer than that calculated from Faraday's law, because some of the current is used in bringing about other decompositions. It is therefore necessary, as a rule, to apply a delicate chemical test to a small portion of the liquid in order to ascertain whether the deposition is complete.

At a temperature 40° to 50° above the ordinary room temperature most depositions take place more rapidly. The saving of time is due to the increased conductivity of the electrolyte, and to the fact that its composition is kept more uniform by the aid of the convection currents which are set up. The platinum basin may be heated by a suitable water-bath, or by a small flame placed several inches below the dish, but the flame must on no account come into direct contact with the basin or the deposit may be loosened. The beaker (Fig. 83) may be heated on a sand-bath or asbestos sheet.

544. Rotating electrodes. When stationary electrodes are employed as described above, the current density must be very small or the deposit of metal will be powdery and non-adherent. But if one of the electrodes be rotated, by means of a water-turbine or small electric motor, at from 30-120 rotations per minute, the C.D. may be very much increased, producing quite firm deposits, and thereby greatly lessening the time required. By this means a deposition may be completed in a few minutes, which would have required several hours with stationary electrodes. The arrangement of the apparatus is shown in Fig. 84. The disc carried on the rotating anode is intended to prevent particles of dirt off the moving parts from falling into the basin.

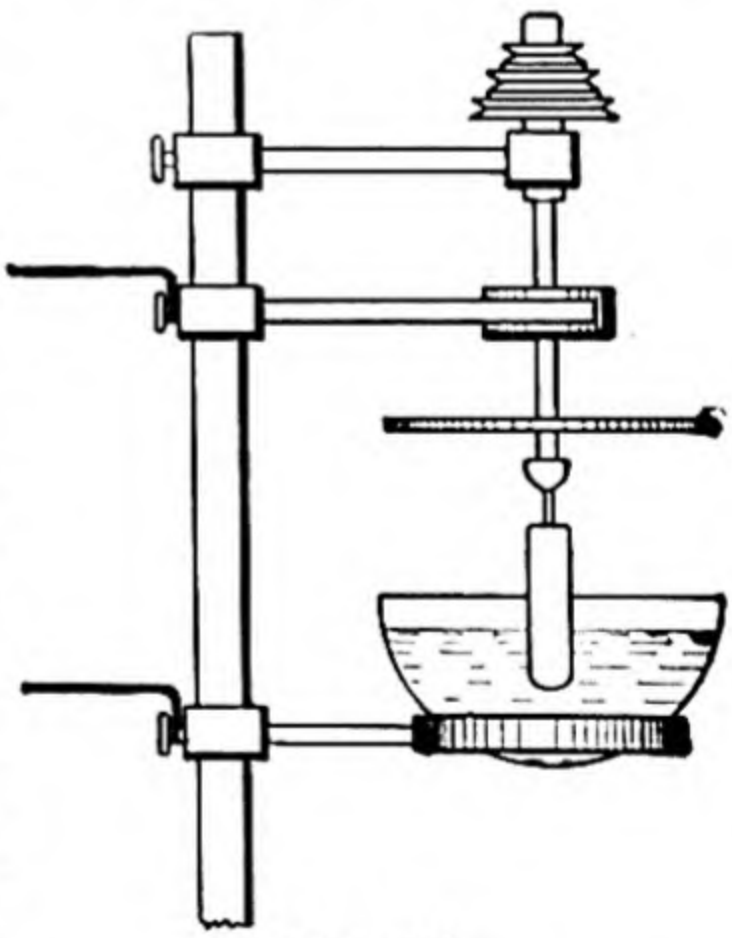


FIG. 84.

545. Estimation of copper. Weigh about 1 g. of copper sulphate into the weighed platinum dish, dissolve in water, and add a little nitric acid. Copper may be deposited in presence of 8–10 per cent. of nitric acid or sulphuric acid. The current density should be 1–1·5 amperes per sq. decimetre at the cathode, the electromotive force 2–2·8 volts, and the time required is about 3 hours, or rather less if the temperature be raised to 50–60°. It is often convenient to carry on a deposition overnight, in which case the C.D. should be reduced to 0·2–0·3 amp. per sq. decimetre, and a little more nitric acid should be added, lest it be all reduced to ammonia. The deposit of copper should be bright red ; too high a C.D. tends to produce a darker-coloured and non-adherent deposit. The addition of about 0·5 g. of hydroxylamine sulphate improves the deposit from solutions containing sulphuric acid, but is not necessary.

When the deposition is judged to be complete, add some water to the solution so that its level is raised 4–5 mm. If, after 15 minutes longer, no film of copper can be seen on the newly covered portion of the cathode, withdraw a little of the solution and test with ferro-cyanide. When no trace of copper can be detected, syphon off the acid liquid, replacing it with distilled water so as to keep the anode covered, then quickly remove the cathode, rinse two or three times with distilled water, then twice with small quantities of alcohol, dry in the steam oven for 5–10 minutes, and weigh as soon as cold.

Copper may always be deposited electrolytically from a solution of the **double cyanide**, $CuK_2(CN)_3$, containing a slight excess of potassium cyanide. A voltage of 2·5 is sufficient, with a C.D. of 0·2–0·5 and a temperature of 15–16°. The experiment is completed as described above.

546. Estimation of zinc. This metal cannot be deposited from solutions which contain more than a trace of mineral acid. The **oxalate method** gives good results. Since the platinum cathode, after dissolving the zinc, is left covered with a film of platinum black, it is better to deposit first a film of copper, or to use nickel electrodes. Weigh about 1 g. of zinc sulphate, dissolve in water

and add 4–5 g. of potassium or ammonium oxalate. Use a C.D. of about 1 ampere, E.M.F. 3·5–4·5, *t* 50–60°. The solution should be kept slightly acid by adding small quantities of oxalic or tartaric acid. To ascertain the end point, test with ferrocyanide.

Cyanide method. A solution of the double cyanide is electrolysed with a C.D. 0·5–1, E.M.F. 4·5–6, *t* 20–50°.

547. Estimation of nickel and cobalt. The most satisfactory method is the electrolysis of an ammoniacal solution of the double sulphate with potassium or ammonium, recommended by Fresenius and Bergmann. Dissolve about 1 g. of the metallic sulphate, add 4–5 g. ammonium or potassium sulphate and 30–40 c.c. ammonia solution. Use a C.D. of 0·5–1·5, E.M.F. 2·5–3·5, *t* 15–50°. Test for the end point with sulphuretted hydrogen.

They may also be estimated by the **cyanide** method as described for copper (545). The **oxalate** method as described for zinc (546) is also applicable.

548. Estimation of iron. Ammonium oxalate gives the best means of depositing iron, and nitrates must be absent. Pour the solution of the iron salt, especially if in the ferrous condition, into a warm solution of an excess of ammonium oxalate. The precipitated iron oxalate should dissolve completely. Use a C.D. of 1–1·5, E.M.F. 3·6–4·3, *t* 15–50°. If a little ferric hydroxide separates during the electrolysis, dissolve it by adding a little oxalic or tartaric acid. A small quantity of borax in the electrolyte improves the deposit. Test for the end point with HCl and KSCN, and wash and dry the deposited iron as rapidly as possible to prevent rusting.

549. Estimation of cadmium. The method described for copper (545) may be used, with a solution *slightly* acid with H_2SO_4. Use 0·5–1 g. of cadmium sulphate, and electrolyse with a C.D. of 0·6–1 ampere, E.M.F. 2·5–3 volts, *t* 50–75°.

The **cyanide** method gives good results, using excess of potassium cyanide. C.D. 0·3–0·5, E.M.F. 3·5–4, *t* 20°.

The end point is ascertained by testing the solution with H_2S.

550. Estimation of silver. The cyanide method gives the best results for silver. The neutral solution of the metal is mixed with excess of a freshly prepared solution of potassium cyanide, and electrolysed. C.D. 0·2–0·5, E.M.F. 3·7–4·8, *t* 20–60°. If allowed to run overnight, the C.D. should be reduced to 0·08–0·15. Ascertain the end by testing a portion with HCl, boiling off HCN.

551. Antimony and tin may be deposited from solutions of the sulpho-salts, the sodium salt being preferable for antimony, and the ammonium salt for tin. For antimony use a C.D. of 1–1·5, E.M.F. 1–1·8, *t* 70–80°; and for tin, C.D. 1–2, E.M.F. 4–4·5, *t* 50–60°.

ANODE DEPOSITS OF PEROXIDE

552. Estimation of lead. Although this metal may be deposited on the cathode, it is difficult to prevent oxidation, and a more convenient method is to deposit the dioxide, PbO_2, on the anode, in presence of at least 10 per cent. of nitric acid. The matt platinum basin may be used as anode. C.D. 1–1·5, E.M.F. 2·5, *t* 15–50°. When completed, wash rapidly with water, then with alcohol, and dry the deposit at 200° until the weight is constant. Chlorides must be absent.

553. Estimation of manganese. A hydrated peroxide of manganese is deposited on the anode from a solution containing 8–10 g. of ammonium acetate and 2–3 g. of chrome alum. The latter prevents the separation of oxygen at the anode, which would loosen the deposit. C.D. 0·6–0·9, E.M.F. 3–4·5, *t* 70–80°. Chlorides must be absent. The deposit after washing is ignited and weighed as Mn_3O_4.

ELECTROLYTIC SEPARATIONS

554. Copper alloys may be examined by the method of electrodeposition, and the copper separated from the other metals by a suitable arrangement either of the E.M.F. or of the chemical composition of the electrolyte. Thus the solution of **brass** or of **bronze** in nitric acid (539) may be made up to 500 c.c., and 100 or 200 c.c. taken for electrolysis. If hydrochloric acid be used in dis-

solving, it must be removed by evaporating with sulphuric or nitric acid. The **copper** may then be deposited from acid solution, in which no zinc, iron, nickel, etc., can come down (**545**). **Lead**, if present, will appear as lead dioxide on the anode, in nitric acid solution (**552**), and is thus determined simultaneously with copper, by weighing the anode also. To obtain the **zinc**, evaporate the acid liquor and washings to dryness in a porcelain dish to remove acid, dissolve in a little hot water, and add excess of ammonium oxalate. Electrolyse as described in par. **546**. As there indicated, the cathode should be filmed with copper before depositing zinc. If **iron** is present in the brass, it will deposit along with the zinc, and may be determined by dissolving the deposit, after weighing, in dilute sulphuric acid, which converts the iron into ferrous sulphate, and then titrating with standard permanganate (**432**).

Silver coinage may be analysed by dissolving in nitric acid and precipitating the silver as chloride (**497**), which may then be weighed as such, or dissolved in KCN solution and electrolysed (**550**). The copper in the filtrate is determined as in par. **545**.

Nickel coinage is dissolved in nitric acid, the copper deposited from this solution (**545**), and the liquor then evaporated with a little H_2SO_4 to remove HNO_3. Concentrated ammonia is added, and the nickel deposited as in par. **547**.

German silver contains copper, zinc and nickel. From the nitric acid solution copper is deposited. Zinc may then be precipitated as ZnS, and the filtrate, after evaporating to remove H_2S, and adding ammonium oxalate, electrolysed for nickel (**547**).

THE NITROMETER AND GAS-VOLUMETER

555. This apparatus affords an easy and rapid method for estimating the volume of gas evolved in various chemical reactions, and was devised by Lunge* for this purpose, with special reference to the analysis of nitrous vitriol. It may be used also for determining the various gases in a mixture, by absorption, since it resembles the Bunte gas burette (**562**).

* *Journ. Soc. Chem. Ind.* 1890, 21.

The apparatus (Fig. 85) consists of a graduated tube *a*, which may be put into communication either with the cup *b* or the side tube *c*. This graduated tube is connected by means of a T-tube and stout rubber tubing to the pressure tube *e* and the reduction tube *r*. The latter is not quite necessary, but was introduced by Lunge * to obviate the calculations otherwise required in the correction of gas volumes for temperature and pressure. It is of great advantage when many samples are analysed consecutively, as in technical work, and its use is simple. The temperature and pressure at the commencement of work are observed. The volume occupied under these conditions by 100 c.c. of dry air is then calculated. This volume of air is introduced into the reduction tube at atmospheric pressure, and the tap at the top of the tube closed. (The top of the tube may terminate in a capillary instead of a tap, and this is sealed off after the air is introduced.) If moist gases are to be measured, and mercury is used in the apparatus, a small drop of water is placed in the reduction tube. When an experiment is made the gas passes into *a*. The level of the liquid in *a* is made equal to that in *e*, and the tap closed; the gas is thus at atmospheric pressure. The three tubes are then adjusted so that the levels of the liquid in *a* and *r* are the same when that in *r* is at the 100 c.c. mark. The gases in *a* and *r* are thus at the same temperature and pressure, and since that in *r* now occupies the volume which it would have at N.T.P., it follows that this is true also of the gas in *a*.

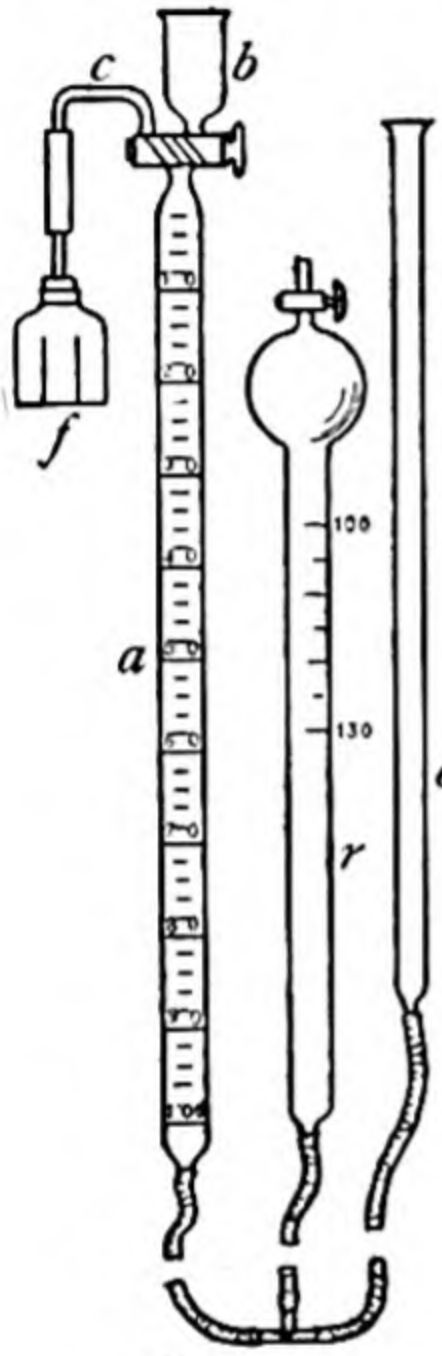


FIG. 85.

The gas burette (Fig. 86) may be used as a gas volumeter for many of the experiments given below, by reversing it so that the tap *d* is at the top, and to this the reaction bottle is attached.

* *Journ. Soc. Chem. Ind.* 1890, 547.

556. Estimation of N_2O_5 in nitrates.

The reaction bottle, *f*, is not used for this experiment.

Fill the apparatus with mercury. In the cup place 0·1 g. of a nitrate and dissolve it in 1 or 2 c.c. of water. Draw this carefully into the nitrometer, without allowing any air to enter. Rinse the cup with 1 c.c. of water, and draw this also into the tube. If any air has got in, raise the pressure tube till it is driven out, but do not send out any of the liquid. Pour into the cup 5 or 6 c.c. of concentrated sulphuric acid, run this into the tube and rinse the cup with 10 c.c. of acid. Remove the tube from the clamp. Turn it horizontally and then quickly back to the vertical position several times. In this way the contents are mixed. Clamp again and allow to stand for 15 to 20 minutes, repeating the mixing at intervals. The sulphuric acid liberates nitric acid, which by the action of the mercury is reduced to nitric oxide. When there is no further increase of volume, bring the gas to atmospheric pressure, by pouring into the pressure tube a quantity of acid, equal and of similar concentration to that in the nitrometer, and equalising the levels. Read the volume of the nitric oxide, and correct for temperature and pressure, or use the reduction tube as already described.

$$KNO_3 \rightarrow NO.$$

$$101 \text{ g.} \rightarrow 22{,}410 \text{ c.c.}$$

$\therefore$ each c.c. of NO corresponds to $\frac{101}{22410} = 0{\cdot}00451$ g. KNO_3.

The decomposition of the nitrate may be carried out in a special decomposition flask instead of in the burette itself, or in another nitrometer, which need not be graduated. When the decomposition is complete, the gas is transferred to the volumeter for measurement.

For experiments other than the analysis of nitrates or of nitrous vitriol, the reaction is carried out in a small flask, or better, in a reaction bottle (Fig. 85, *f*).

The reaction bottle is a wide-mouthed bottle with a wide cylindrical tube inside, sealed to the bottom. To avoid raising the temperature, it should be handled only by the neck, with the thumb and forefinger.

557. Estimation of CO_2 in a carbonate. Weigh 0·3 g. of Iceland spar into the outer portion of the bottle, and place 10 c.c. of hydrochloric acid (sp. gr. 1·125) in the inner portion. Connect the bottle to the graduated tube, equalise the levels, then turn the tap to connect the tube with the cup, i.e. to the atmosphere, and fill the tube with liquid by raising the pressure tube. On turning the tap again to put the tube in communication with the bottle, no air should enter the graduated tube, as the gas in the bottle was already brought to the atmospheric pressure.

Now tilt the bottle to mix the acid and the carbonate, and the gas evolved will pass into *a*. The pressure tube should be lowered during the evolution of the gas, so as to reduce the pressure. When the reaction is over, adjust the levels, and read the volume. Water may be used in the apparatus without much loss, but a correction should be made for the volume of CO_2 dissolved by the acid. According to Scheibler, 10 c.c. of acid (sp. gr. 1·125) absorb 8·2 c.c. of CO_2 at 16° C.

558. Estimation of hydrogen peroxide in solution. Place 2 c.c. of hydrogen peroxide in the inner compartment, and excess of potassium permanganate solution and sulphuric acid in the outer. Shake the bottle vigorously so that all the hydrogen peroxide reacts :

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$
$$5O + 5H_2O_2 = 5H_2O + 5O_2.$$

Half the oxygen collected comes from the peroxide, and this, after correction for temperature and pressure, gives the volume of oxygen from 2 c.c. of the solution. Repeat the experiment in order to confirm the result. The method is very accurate. Compare the titration method, par. 438.

Standardisation of potassium permanganate solution. By using a known volume of potassium permanganate solution, acidified with sulphuric acid, and excess of peroxide, the strength of the permanganate may be found. The method is exactly like that in the previous experiment.

559. Valuation of commercial manganese dioxide. Weigh 0·2 g. of the finely powdered oxide into the outer compartment, and add a few c.c. of sulphuric acid (1 : 1). In the inner compartment place excess of hydrogen peroxide. The manganese dioxide should dissolve completely on mixing, leaving only a slightly coloured residue of silica and other insoluble matter. As before, half the oxygen evolved comes from the manganese dioxide :

$$MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + 2H_2O + O_2.$$

560. Valuation of bleaching powder. Weigh 0·5 g. into the outer compartment and add a little water. Hydrogen peroxide is placed in the inner compartment, but should not be in large excess :

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

Since the residual liquid is alkaline, the volume of gas should be read as soon as the rapid reaction is over, say after 5 minutes ; the excess of hydrogen peroxide will decompose slowly, liberating oxygen. This remark applies also to the next experiment.

561. Estimation of $K_3Fe(CN)_6$ in the crystals. Weigh 1·5 g. into the outer compartment, add to it excess of alkali hydroxide and place excess of peroxide in the inner compartment :

$$\underset{598}{2K_3Fe(CN)_6} + 2KOH + H_2O_2 = 2K_4Fe(CN)_6 + 2H_2O + \underset{32}{O_2}.$$

$\therefore$ 598 g. correspond to 22,410 c.c. of oxygen liberated.

GAS ANALYSIS

562. The analysis of a mixture of gases is usually carried out by means of a gas-burette and pipettes.

The Hempel burette (Fig. 86) has an ordinary tap at the top, and at the bottom a three-way tap *d*, so that it may be connected either with the pressure tube or with the atmosphere.

The burette is filled with liquid (generally water saturated with the gas to be tested, or, for more accurate work, with mercury), and connected to the vessel containing the gas to be analysed. By lowering the pressure tube, the gas may be drawn

into the burette if suitable provision be made to allow liquid to enter the vessel as the gas is withdrawn. If coal gas is to be examined, the lower tap is turned so as to connect the burette with the atmosphere, the top of the burette is connected to the gas tap, and the gas allowed to sweep out all the air. Having filled the burette, it is now connected to the pipette.

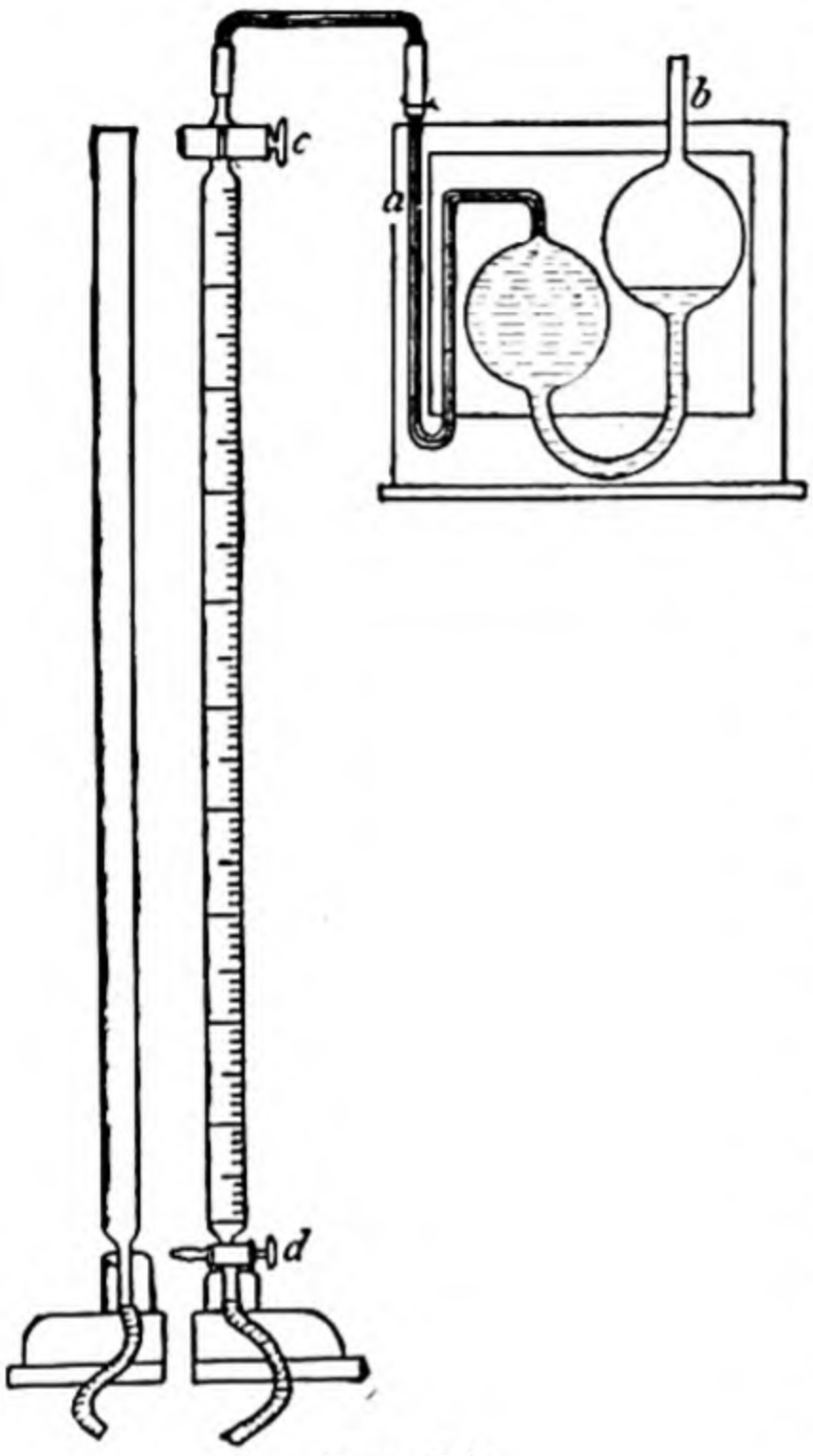


FIG. 86.

The simplest form of Hempel pipette (Fig. 86) consists of two bulbs in communication, the lower of which terminates in a bent tube of small bore, *a*. A piece of stout rubber tubing is wired on to the end of this, and closed by a pinch clip.

When the pipette is not in use, it is closed by pieces of rubber tubing fitted with glass rods.

The pipette is filled, by means of the tube *b*, with a liquid which absorbs one of the gases to be estimated. The quantity of liquid is such that when it is brought to a mark near the top of the tube *a*, the lower bulb is full and there is a small quantity in the upper bulb. The various gases are absorbed as follows :

Carbon dioxide by potassium hydroxide. Dissolve 160 g. of potassium hydroxide in 130 c.c. of water. This solution also absorbs all acid-forming gases, as HCl, H_2S, SO_2 : the latter may also be absorbed by iodine solution, while **chlorine**, in presence of CO_2, may be removed by potassium iodide or ferrous chloride solution.

Oxygen by alkaline pyrogallol. Dissolve 10 g. of pyrogallol in 200 c.c. of the above potassium hydroxide solution.

Carbon monoxide by cuprous chloride solution. Carbon monoxide may be absorbed by either an acid or an ammoniacal solution, the latter being used when the combustion of hydrogen by palladinised asbestos is subsequently to be carried out.

Acid cuprous chloride solution is prepared by dissolving 27 g. of cuprous chloride in 200 c.c. of hydrochloric acid, sp. gr. 1·124.

Ammoniacal cuprous chloride solution is prepared by suspending 15 g. of cuprous chloride in 120 c.c. of water in a 250 c.c. flask and passing ammonia gas into the liquid until all the solid is dissolved.

Acetylene by ammoniacal cuprous chloride.

The olefines by bromine water or fuming sulphuric acid.

Nitric oxide by ferrous sulphate solution. Use a cold saturated solution.

Nitrous oxide by means of alcohol: this, however, is only approximate.

Ammonia by dilute sulphuric acid.

Hydrogen is estimated by explosion with excess of air in a special explosion pipette (Fig. 87), or the union of the hydrogen and oxygen may be brought about by palladinised asbestos.

Methane is estimated by explosion with oxygen. The volume of **nitrogen** is obtained by difference.

To carry out an absorption, attach the burette to the pipette, containing the required liquid, by a piece of small-bore glass tubing bent twice at right angles (Fig. 86). Remove the clip from the pipette. The liquid will remain at the mark on the tube *a*, if the apparatus is air-tight. Open the tap *c*, and turn the lower tap *d*, to connect the burette with the pressure tube, and by raising the latter transfer the whole of the gas into the pipette. Close the tap *c*, and allow the gas to remain in contact with the liquid for five minutes, shaking the pipette gently with a circular motion. Then open *c* and *d* and withdraw the gas until the liquid in the pipette reaches the mark on the tube, close *c*, adjust the pressure and read the volume. Again pass the gas into the pipette to see whether the absorption is complete.

When there is no further decrease in volume read off the volume of the gas absorbed.

Now attach the second pipette, then the third, and so on until the absorptions are completed.

The order of absorption is important, and will depend upon the composition of the gas-mixture. Sulphur dioxide may be absorbed by iodine solution (decinormal) or a saturated solution of potassium dichromate, and must be determined before the carbon dioxide. If ethylene is absorbed by bromine water, the gas should next be passed into the potassium hydroxide pipette to free it from bromine vapour.

After the simple absorptions of CO_2, O_2, etc., hydrogen, methane and other saturated hydrocarbons and nitrogen remain. This residual gas is mixed with excess of air in the burette and the volume read. It is then passed into a pipette containing water only, through a glass tube of fine bore containing a fibre of palladinised asbestos. This tube is heated gently during the passage of the gas. The hydrogen unites with oxygen, but the methane is not affected :

$$\underset{\text{2 vols.}}{2H_2} + \underset{\text{1 vol.}}{O_2} = 2H_2O.$$

The gas is brought back into the burette, and when there is no further decrease in volume, two-thirds of the decrease gives the volume of the hydrogen.

The gas now contains methane, nitrogen and a known volume of oxygen and nitrogen from the air added. An excess of oxygen is now added, and the gas is passed into an explosion pipette filled with mercury (Fig. 87), and exploded by sparking. To prevent loss of gas during firing, the rubber tube should be wired on to *a* and closed by a screw clip.

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + 2H_2O.$$

The decrease in volume is twice the volume of the methane, which is equal to the volume of carbon dioxide produced. The carbon dioxide may be measured by absorption in the potassium hydroxide pipette.

The hydrogen and the methane in the mixture may also be determined conjointly by the explosion pipette, by noting the decrease in volume, and measuring the volume of carbon dioxide produced. Let the volume of the methane be x. This is equal to

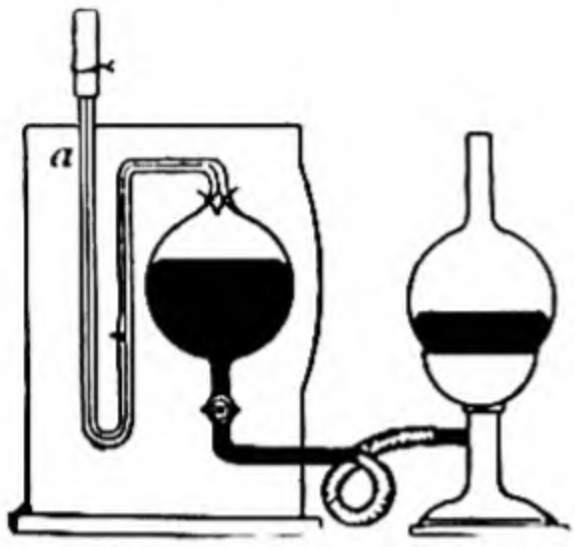


FIG. 87. Explosion pipette.

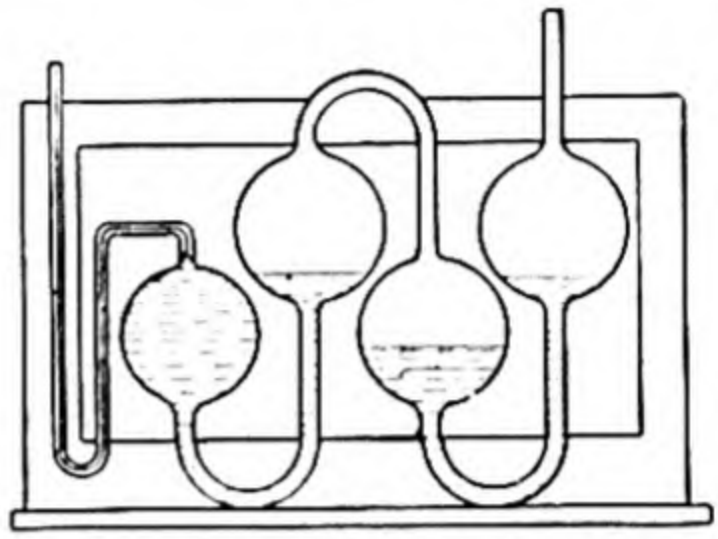


FIG. 88. Double pipette.

that of the carbon dioxide produced. $2x$ will be the volume of oxygen lost by the burning of the methane. The only other loss is that caused by the union of free hydrogen with oxygen, which is therefore equal to the decrease in volume less $2x$; two-thirds of this volume gives the hydrogen.

Certain liquids used for absorption should be kept as much as possible from the air, e.g. pyrogallol, or ammoniacal cuprous chloride; and for these a double pipette (Fig. 88) is used. The additional bulbs act as a water seal and prevent contact of air with the reagent. An inert gas fills that portion of the pipette between the reagent and the water.

563. The Orsat apparatus is a compact and portable arrangement of burette and pipettes designed for the rapid examination of a gas. The burette, which has a capacity of 100 c.c. and is surrounded by a water-jacket, consists of a cylindrical bulb continued beneath in a graduated tube of uniform bore, and ending in a tap outside of the jacket. The tap is connected by rubber tube with a level-bottle, by means of which the gas can be passed to and fro as required. From the upper end of the burette a capillary passes horizontally to connect by means of three-way taps with the various pipettes. These have the form of double cylinders, arranged as U-tubes, the farther end of each being

closed when not in use. The whole apparatus is fixed for support in a wooden frame. The treatment of the gas is similar to that applied in the Hempel apparatus.

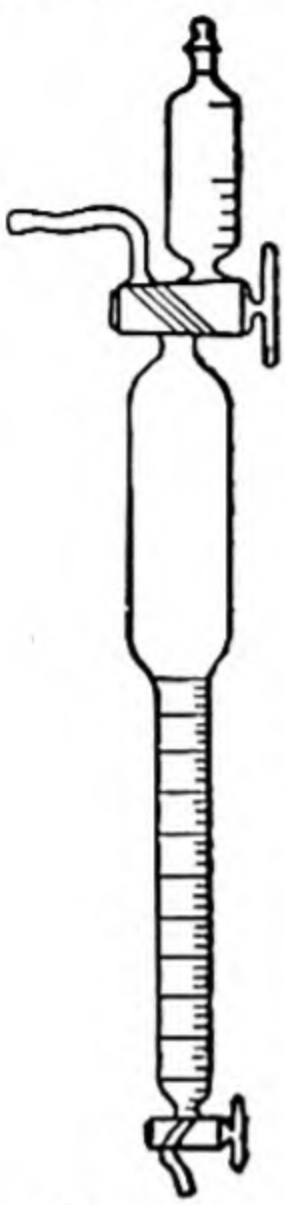


FIG. 89.

Bunte's gas burette affords a simple method of carrying out absorptions in the burette itself (Fig. 89). It resembles the nitrometer (**555**), with which it may be interchanged, but it has a tap also at the bottom. The gas to be analysed is passed into the burette, and the absorbent liquid introduced from the cup, which has marks for 20–25 c.c. When the absorption is complete, the volume is read, the liquid drawn off at the bottom, and after rinsing the burette with a little water, the next absorbent is introduced.

For practice in the use of the Hempel and other apparatus, the following gas-mixtures may be analysed: the air in the laboratory, air from the lungs, coal gas, flue gas, H_2S in the laboratory supply, the gas from oxalic acid, etc.

APPENDIX

APPENDIX

564. Atomic Weights (1937) and other Constants.

Element	Symbol	At. No.	At. Wt. O = 16	D. g. per c.c.	Sp. Ht.	M.P.	B.P.
Actinium	Ac	89	227	—	—	—	—
Aluminium	Al	13	26·97	2·703	0·214	659	1,800
Antimony	Sb	51	121·76	6·7	0·051	630	1,635
Argon	A	18	39·944	*0·0$_2$17809*	—	−189·3	−186
Arsenic	As	33	74·91	5·73	0·083	554	—
Barium	Ba	56	137·36	3·78	0·068	850	—
Beryllium	Be	4	9·02	1·85	0·0425	1,280	1,500
Bismuth	Bi	83	209·0	9·8	0·0308	271	1,436
Boron	B	5	10·82	2·54	0·307	2,500?	—
Bromine	Br	35	79·916	3·12	0·107	−73	63
Cadmium	Cd	48	112·41	8·65	0·0567	321	778
Caesium	Cs	55	132·91	1·87	0·048	26·4	670
Calcium	Ca	20	40·08	1·548	0·149	810	1,710
Carbon	C	6	12·01	3·51	0·17	—	—
Cerium	Ce	58	140·13	7·02	0·0448	635	—
Chlorine	Cl	17	35·457	*0·0$_2$32204*	—	−102	−34
Chromium	Cr	24	52·01	6·92	0·112	1,615	2,200
Cobalt	Co	27	58·94	8·72	0·1035	1,480	—
Copper	Cu	29	63·57	8·95	0·093	1,084	2,310
Dysprosium	Dy	66	162·46	—	—	—	—
Erbium	Er	68	167·64	—	—	—	—
Europium	Eu	63	152·00	—	—	—	—
Fluorine	F	9	19·00	*0·0$_2$1694*	—	−233	−188
Gadolinium	Gd	64	156·9	—	—	—	—
Gallium	Ga	31	69·72	5·94	0·080	30	—
Germanium	Ge	32	72·60	5·5	0·074	958	—
Gold	Au	79	197·2	19·3	0·031	1,064	2,500
Hafnium	Hf	72	178·6	13·3	—	2,230	—
Helium	He	2	4·002	*0·0$_3$17856*	—	−272	−268·8
Holmium	Ho	67	163·5	—	—	—	—
Hydrogen	H	1	1·0078	*0·0$_4$89873*	—	−259	−252
Illinium	Il	61	—	—	—	—	—
Indium	In	49	114·76	7·28	0·0323	155	—
Iodine	I	53	126·92	4·94	0·054	114	183
Iridium	Ir	77	193·1	22·42	0·0323	2,360	—
Iron	Fe	26	55·84	7·86	0·113	1,533	2,450
Krypton	Kr	36	83·7	*0·0$_2$3708*	—	−157	−102
Lanthanum	La	57	138·92	6·155	0·045	810	—
Lead	Pb	82	207·21	11·4	0·0305	327	1,525
Lithium	Li	3	6·940	0·59	1·093	186	1,400
Lutecium	Lu	71	175·0	—	—	—	—
Magnesium	Mg	12	24·32	1·74	0·248	632	1,120

Element	Symbol	At. No.	At. Wt. O = 16	D. g. per c.c.	Sp. Ht.	M.P.	B.P.
Manganese	Mn	25	54·93	7·06	0·122	1,230	1,900
Masurium	Ma	43	—	—	—	—	—
Mercury	Hg	80	200·61	13·515	0·033	−39	357
Molybdenum	Mo	42	96·0	9·01	0·072	2,535	3,620
Neodymium	Nd	60	144·27	6·96	—	840	—
Neon	Ne	10	20·183	$0{\cdot}0_3 9002$	—	−253	−239
Nickel	Ni	28	58·69	8·85	0·109	1,452	—
Niobium	Nb	41	92·91	7·3	—	1,950	—
Nitrogen	N	7	14·008	$0{\cdot}0_2 12507$	—	−210	−195
Osmium	Os	76	191·5	22·48	0·0311	2,700	—
Oxygen	O	8	16·000	$0{\cdot}0_2 14290$	—	−219	−183
Palladium	Pd	46	106·7	11·7	0·0592	1,550	2,540
Phosphorus	P	15	31·02	1·83	0·202	44	288
Platinum	Pt	78	195·23	21·42	0·0325	1,750	—
Polonium	Po	84	210	—	—	—	—
Potassium	K	19	39·096	0·875	0·166	62·3	76
Praseodymium	Pr	59	140·92	6·48	—	940	—
Protoactinium	Pa	91	230	—	—	—	—
Radium	Ra	88	226·05	6·0	—	700	—
Radon	Rn	86	222	—	—	—	—
Rhenium	Re	75	186·31	21·4	—	3,440	—
Rhodium	Rh	45	102·91	12·44	0·058	1,950	—
Rubidium	Rb	37	85·48	1·52	—	38·5	646
Ruthenium	Ru	44	101·7	12·06	0·061	2,450	—
Samarium	Sa	62	150·43	7·7	—	1,350	—
Scandium	Sc	21	45·10	3·9	—	1,200	—
Selenium	Se	34	78·96	4·28	0·084	217	688
Silicon	Si	14	28·06	2·46	0·181	1,420	—
Silver	Ag	47	107·880	10·5	0·056	961	1,955
Sodium	Na	11	22·997	0·971	0·293	97·5	880
Strontium	Sr	38	87·63	2·5	—	752	1,640
Sulphur	S	16	32·06	1·96	0·174	115	445
Tantalum	Ta	73	180·88	16·6	0·033	2,800	—
Tellurium	Te	52	127·61	5·93	0·0483	452	1,390
Terbium	Tb	65	159·2	—	—	—	—
Thallium	Tl	81	204·39	11·88	0·0326	302	1,280
Thorium	Th	90	232·12	11·2	0·0276	1,700	—
Thulium	Tm	69	169·4	—	—	—	—
Tin	Sn	50	118·7	7·2	0·055	232	2,270
Titanium	Ti	22	47·90	4·5	0·113	1,850	—
Tungsten	W	74	184·0	18·7	0·034	3,400	—
Uranium	U	92	238·14	18·7	0·028	1,850	—
Vanadium	V	23	50·95	5·69	0·115	1,720	—
Xenon	Xe	54	131·3	$0{\cdot}0_2 5851$	—	−112	−107
Ytterbium	Yb	70	173·04	6·9	—	—	—
Yttrium	Y	39	88·92	3·8	—	1,490	2,500
Zinc	Zn	30	65·38	7·1	0·093	420	920
Zirconium	Zr	40	91·22	4·19	0·066	2,350	—
Eka-Iodine	—	85	—	—	—	—	—
Eka-Caesium	—	87	—	—	—	—	—

565. Table of Solubilities.

1 = Soluble in water.

2 = Sparingly soluble in water ; soluble in dilute acids.

	$K^{\cdot}$	$Na^{\cdot}$	$Li^{\cdot}$	$NH_4^{\cdot}$	$Mg^{\cdot\cdot}$	$Ca^{\cdot\cdot}$	$Sr^{\cdot\cdot}$	$Ba^{\cdot\cdot}$	$Fe^{\cdot\cdot}$	$Fe^{\cdot\cdot\cdot}$	$Cr^{\cdot\cdot\cdot}$	$Al^{\cdot\cdot\cdot}$	$Zn^{\cdot\cdot}$
Cl'	1	1	1	1	1	1	1	1	1	1	1	1	1
Br'	1	1	1	1	1	1	1	1	1	1	1	1	1
I'	1	1	1	1	1	1	1	1	1	1	1	1	1
Fl'	1	1	1	1	4	4	4	4	2	1	1	1	2
ClO'	All hypochlorites are soluble in water.												
ClO_3'	All chlorates are soluble in water.												
CN'	1	1	1	1	1	1	1	2	4	–	3	–	3
$Fe(CN)_6''''$	1	1	1	1	1	1	1	2	4	4	–	–	4
$Fe(CN)_6'''$	1	1	1	1	1	1	–	–	4	1	–	–	4
O''	1	1	1	1	3	2	2	1	3	3	3	3	3
S''	1	1	1	1	1	1	1	1	3	3	3	3	3
SO_3''	1	1	1	1	1	All other sulphites							
SO_4''	1	1	1	1	1	4	4	5	1	1	1	1	1
S_2O_3''	1	1	1	1	1	1	1	2	1	1	1	1	1
CO_3''	1	1	2	1	3	3	3	2	All other carbon				
SiO_3''	1	1	1	–	All other silicates solu								
NO_2''	All nitrites soluble in												
NO_3''	All nitrates soluble in												
PO_4'''	1	1	2	1	All other phosphates								
AsO_3'''	1	1	1	1	All other arsenites								
AsO_4'''	1	1	1	1	All other arsenates								
BO_3'''	1	1	1	1	All other borates								
CrO_4''	1	1	1	1	1	2	2	3	–	1	3	–	1
MnO_4'	All other permanganates are soluble												
CH_3COO' §	All acetates soluble in water.												
$(COO)_2''$	1	1	1	1	All other oxalates solubility 2.								
$C_4H_4O_6''$	1	1	1	1	2	2	2	2	1	1	1	1	2

* Readily soluble in hot water.

† Decomposed by water into basic compounds of solubility 3.

3 = Insoluble in water ; soluble in acids.

4 = Insoluble in water ; difficultly soluble in acids.

5 = Insoluble in water or acids.

$Mn^{''}$	$Ni^{''}$	$Co^{''}$	$Sb^{'''}$	$Sn^{''}$	$Sn^{''''}$	$Pb^{''}$	$Hg^{'}$	$Hg^{''}$	$Ag^{'}$	$Bi^{'''}$	$Cu^{''}$	$Cd^{''}$	
1	1	1	1†	1	1	1*	4	1	5	1†	1	1	$Cl^{'}$
1	1	1	1†	–	–	1*	3	1	5	2	1	1	$Br^{'}$
1	1	1	2	1	1	1*	2	2	5	3	1	1	$I^{'}$
3	2	2	1	1	1	3	–	2	1	1	3	2	$Fl^{'}$
													$ClO^{'}$
													$ClO_3^{'}$
3	4	4	–	–	–	3	–	1	5	–	4	3	$CN^{'}$
3	5	5	–	–	5	3	–	–	5	–	5	–	$Fe(CN)_6^{''''}$
3	5	5	–	–	–	2	–	–	5	–	–	–	$Fe(CN)_6^{'''}$
3	3	3	3	3	4	3	3	3	3	3	3	3	$O^{''}$
3	3‡	3‡	3	3	3	3	–	3‡	3	3	3	3	$S^{''}$
soluble in acids.													$SO_3^{''}$
1	1	1	3	1	–	4	2	1	2	1	1	1	$SO_4^{''}$
1	1	1	1	1	1	2	1	1	2	1	1	1	$S_2O_3^{''}$
ates solubility 3.													$CO_3^{''}$
bility 3.													$SiO_3^{''}$
water.													$NO_2^{''}$
water.													$NO_3^{''}$
soluble in acids.													$PO_4^{'''}$
soluble in acids.													$AsO_3^{'''}$
soluble in acids.													$AsO_4^{'''}$
soluble in acids.													$BO_3^{'''}$
1	3	3	–	–	–	4	3	2	3	3	1	1	$CrO_4^{''}$
in water.			–	–	–	–	–	–	2	–	–	–	$MnO_4^{'}$
													$CH_3COO^{'}$ §
													$(COO)_2^{''}$
2	1	1	1	1	1	2	2	2	2	1	2	2	$C_4H_4O_6^{''}$

‡ Soluble only in aqua regia.

§ Fe, Al, Pb, Cu also form basic acetates, solubility 2.

566. Table of solubilities.

The data in this table are taken chiefly from Comey's *Dictionary of Chemical Solubilities.*

Substance	100 parts water dissolve at			
	0°	20°	50°	100°
Aluminium sulphate, $Al_2(SO_4)_3 . 18H_2O$	86·85	107·35	201·4	1132
,, ,, anhydrous *	31·3	36·15	52·13	89·11
Potash alum, $KAl(SO_4)_2 . 12H_2O$	3·9	15·13	44·11	357·5
Ammonium alum, $(NH_4)Al(SO_4)_2 . 12H_2O$	5·22	13·66	36·5	421·9
Antimonyl potass. tartrate, $K(SbO)C_4H_4O_6$	5·26 (8·7°)	7·94 (21°)	18·18	35·71
Ammonium chloride, NH_4Cl	28·4	37·28	50·60	72·80
,, sulphate, $(NH_4)_2SO_4$	70·6	75·4	84·4	103·3
,, nitrate, NH_4NO_3	—	199·2 (18°)	—	—
Barium chloride, $BaCl_2$	30·9	35·7	43·6	58·8
,, hydroxide, $Ba(OH)_2$	1·5	3·48	11·75	90·77 (80°)
Borax, $Na_2B_4O_7 . 10H_2O$	2·83	7·88	27·41	201·43
Bromine	3·60 (5°)	3·327 (10°)	3·208 (20°)	3·126 (30°)
Calcium chloride, $CaCl_2$	49·6	74	120	155
,, sulphate, $CaSO_4$	0·205	0·241	0·251	0·217
,, hydroxide, $Ca(OH)_2$	0·131	0·126	0·098	0·060
Chlorine, c.c. in 1 c.c. water	2·5825 (10°)	2·1565	1·3655 (40°)	—
Chrome alum, $KCr(SO_4)_2 . 12H_2O$	soluble in	6–7 parts	cold water	
Cupric sulphate, $CuSO_4 . 5H_2O$	31·61	42·31	65·83	203·32
Ferrous sulphate, $FeSO_4$	7·9	24·7	51·9	42·6
,, ammon. sulphate, $Fe(NH_4)_2(SO_4)_2$	12·2	21·6	38·2	56·7 (75°)
Ferric alum, $(KFe(SO_4)_2 . 12H_2O$	—	33·3 (15°)	—	—
Lead nitrate, $Pb(NO_3)_2$	36·5	52·3	78·7	127
,, chloride, $PbCl_2$	0·8	1·18	2·0	3·1 (80°)
,, acetate, $Pb(C_2H_3O_2)_2$	—	48	—	70
Magnesium sulphate, $MgSO_4$	26·9	36·2	50·3	73·8
,, chloride, $MgCl_2$	52·2	200 (15·5)	—	—
Manganous sulphate, $MnSO_4$	55·4	66·3	74·8	52·9
Mercuric chloride, $HgCl_2$	5·73	7·39	11·34	53·96

* Where no water of crystallisation is mentioned, the solubility is that of the anhydrous salt.

TABLE OF SOLUBILITIES—*Continued.*

Substance	100 parts water dissolve at			
	0°	20°	50°	100°
Nickel sulphate, $NiSO_4$	29·3	39·0	54·5	83·7
,, ammonium sulphate, $Ni(NH_4)_2(SO_4)_2$	1·8 (3·5°)	5·9	14·4	28·6 (85°)
Potassium chloride, KCl	28·5	34·7	42·8	56·6
,, bromide, KBr	53·48	64·52	80·0	102·0
,, iodide, KI	127·9	144·2	168	209
,, nitrate, KNO_3	13·3	31·2	86·0	247
,, sulphate, K_2SO_4	8·5	10·9	15·8	126·2
,, carbonate, K_2CO_3	83·12	94·06	112·90	153·66
,, chlorate, $KClO_3$	3·33	7	19	60
,, perchlorate, $KClO_4$	0·70	—	6·45	19·90
,, bromate, $KBrO_3$	3·11	6·92	22·76 (60°)	49·75
,, chromate, K_2CrO_4	58·9	62·94	69·0	79·10
,, dichromate, $K_2Cr_2O_7$	4·6	12·4	35·0	94·1
,, permanganate, $KMnO_4$	—	6·25 (15°)	—	—
Silver nitrate, $AgNO_3$	122	228	500 (54°)	940
Sodium chloride, NaCl	35·52	35·6	37·0	39·61
,, nitrate, $NaNO_3$	72·9	87·5	112	180
,, sulphate, Na_2SO_4	4·8	19·5	46·7	42·5
,, carbonate, $Na_2CO_3 . 10H_2O$	21·3	92·8	1,142 (38°)	540
,, bicarbonate, $NaHCO_3$	6·9	9·6	14·45	16·7 (70°)
,, phosphate, Na_2HPO_4	2·5	9·3	82·5	98·8
,, sulphite, Na_2SO_3	14·1	25·8	49·5 (40°)	—
,, thiosulphate, $Na_2S_2O_3$	47·6	69·5	140·0	192 (60°)
Strontium chloride, $SrCl_2$	44·2	53·9	74·4	101·9
,, hydroxide, $Sr(OH)_2$	0·35	0·68	2·13	18·60
Stannous chloride, $SnCl_2$	83·9	269·8 (15°)	—	—
Sulphur dioxide, c.c. in 1 c.c. water	79·789	39·374	18·77 (40°)	—
Sulphuretted hydrogen, c.c. in 1 c.c. water	4·37	2·91	1·857 (40°)	—
Zinc sulphate, $ZnSO_4 . 7H_2O$	115·22	161·5	263·84	653·6

567. Sulphuric acid.

Specific gravity and concentration of its solutions.
(Lunge and Isler.) Temperature 15/4.

Specific gravity	% H_2SO_4	Specific gravity	% H_2SO_4	Specific gravity	% H_2SO_4	Specific gravity	% H_2SO_4
1·005	0·83	1·240	32·28	1·480	57·83	1·720	78·92
1·020	3·03	1·260	34·57	1·500	59·70	1·740	80·68
1·040	5·96	1·280	36·87	1·520	61·59	1·760	82·44
1·060	8·77	1·300	39·19	1·540	63·43	1·780	84·50
1·080	11·60	1·320	41·50	1·560	65·08	1·800	86·90
1·100	14·35	1·340	43·74	1·580	66·71	1·820	90·05
1·120	17·01	1·360	45·88	1·600	68·51	1·827	91·50
1·140	19·61	1·380	48·00	1·620	70·32	1·834	93·05
1·160	21·19	1·400	50·11	1·640	71·99	1·839	95·00
1·180	24·76	1·420	52·15	1·660	73·64	1·8415	97·00
1·200	27·32	1·440	54·07	1·680	75·42	1·8400	98·70
1·220	29·84	1·460	55·97	1·700	77·17	1·8385	99·95

568. Hydrochloric acid.

Concentration and specific gravity of its solutions.
(Kolb, recalculated by Gerlach.) Temperature 15/0.

% HCl	Specific gravity	% HCl	Specific gravity	% HCl	Specific gravity	% HCl	Specific gravity
0	0·9992	11	1·05529	22	1·11058	33	1·16587
1	1·00503	12	1·06031	23	1·11560	34	1·17089
2	1·01005	13	1·06534	24	1·12063	35	1·17592
3	1·01508	14	1·07037	25	1·12566	36	1·18095
4	1·02010	15	1·07539	26	1·13068	37	1·18597
5	1·02513	16	1·08042	27	1·13571	38	1·191
6	1·03016	17	1·08545	28	1·14074	39	1·196
7	1·03518	18	1·09047	29	1·14516	40	1·200
8	1·04021	19	1·09550	30	1·15079	41	1·204
9	1·04524	20	1·10052	31	1·15581	42	1·208
10	1·05026	21	1·10555	32	1·16084	43	1·212

569. Nitric acid.

Specific gravity and concentration of its solutions.
(Lunge and Rey.) Temperature 15/4.

Specific gravity	% HNO_3	Specific gravity	% HNO_3	Specific gravity	% HNO_3	Specific gravity	% HNO_3
1·000	0·10	1·165	27·12	1·330	52·37	1·475	84·45
1·015	2·80	1·185	30·13	1·345	54·93	1·485	87·70
1·030	5·50	1·205	33·09	1·360	57·57	1·500	94·09
1·045	8·13	1·215	34·55	1·375	60·30	1·504	96·00
1·060	10·68	1·225	36·03	1·390	63·23	1·506	96·76
1·075	13·15	1·245	39·05	1·400	65·30	1·508	97·50
1·090	15·53	1·260	41·34	1·410	67·50	1·510	98·10
1·105	17·89	1·280	44·41	1·420	69·80	1·512	98·53
1·125	21·00	1·290	45·95	1·430	72·17	1·515	99·07
1·140	23·31	1·305	48·26	1·445	75·98	1·517	99·34
1·150	24·84	1·320	50·71	1·460	79·98	1·520	99·67

570. Ammonia.

Specific gravity and concentration of its solutions.
(Lunge and Wiernik.) Temperature 15°.

Specific gravity	% NH_3	Specific gravity	% NH_3	Specific gravity	% NH_3	Specific gravity	% NH_3
1·000	0·00	0·970	7·31	0·940	15·63	0·910	24·99
0·998	0·45	0·968	7·82	0·938	16·22	0·908	25·65
0·996	0·91	0·966	8·33	0·936	16·82	0·906	26·31
0·994	1·37	0·964	8·84	0·934	17·42	0·904	26·98
0·992	1·84	0·962	9·35	0·932	18·03	0·902	27·65
0·990	2·31	0·960	9·91	0·930	18·64	0·900	28·33
0·988	2·80	0·958	10·47	0·928	19·25	0·898	29·01
0·986	3·30	0·956	11·03	0·926	19·87	0·896	29·69
0·984	3·80	0·954	11·60	0·924	20·49	0·894	30·37
0·982	4·30	0·952	12·17	0·922	21·12	0·892	31·05
0·980	4·80	0·950	12·74	0·920	21·75	0·890	31·75
0·978	5·30	0·948	13·31	0·918	22·39	0·888	32·50
0·976	5·80	0·946	13·88	0·916	23·03	0·886	33·25
0·974	6·30	0·944	14·46	0·914	23·68	0·884	34·10
0·972	6·80	0·942	15·04	0·912	24·33	0·882	34·95

71. Tension of water vapour.

(Regnault.)

Temp. C.	Tension mm.	Temp. C.	Tension mm.	Temp. C.	Tension mm.	Temp. C.	Tension mm.	Temp. C.	Tension mm.
−2·0	3·9	4·5	6·3	11·0	9·8	17·5	14·9	24·0	22·2
−1·5	4·1	5·0	6·5	11·5	10·1	18·0	15·4	24·5	22·9
−1·0	4·3	5·5	6·8	12·0	10·5	18·5	15·8	25·0	23·6
−0·5	4·4	6·0	7·0	12·5	10·8	19·0	16·3	25·5	24·3
0·0	4·6	6·5	7·2	13·0	11·2	19·5	16·9	26·0	25·0
+0·5	4·8	7·0	7·5	13·5	11·5	20·0	17·4	26·5	25·7
1·0	4·9	7·5	7·7	14·0	11·9	20·5	17·9	27·0	26·5
1·5	5·1	8·0	8·0	14·5	12·3	21·0	18·5	27·5	27·3
2·0	5·3	8·5	8·3	15·0	12·7	21·5	19·1	28·0	28·1
2·5	5·5	9·0	8·6	15·5	13·1	22·0	19·7	28·5	28·9
3·0	5·7	9·5	8·9	16·0	13·5	22·5	20·3	29·0	29·8
3·5	5·9	10·0	9·2	16·5	14·0	23·0	20·9	29·5	30·7
4·0	6·1	10·5	9·5	17·0	14·4	23·5	21·5	30·0	31·5

572. Water.

Density and volume at different temperatures.

(Volkmann.)

t	Weight of 1 c.c. water in g.	Volume of 1 g. water in c.c.	*t*	Weight of 1 c.c. water in g.	Volume of 1 g. water in c.c.
0	0·999878	1·000122	14	0·999297	1·000703
1	0·999933	1·000067	15	0·999154	1·000847
2	0·999972	1·000028	16	0·999004	1·000997
3	0·999993	1·000007	17	0·998839	1·001162
4	1·000000	1·000000	18	0·998663	1·001339
5	0·999992	1·000008	19	0·998475	1·001527
6	0·999969	1·000031	20	0·998272	1·001731
7	0·999933	1·000067	21	0·998065	1·001939
8	0·999882	1·000118	22	0·997849	1·002156
9	0·999819	1·000181	23	0·997623	1·002383
10	0·999739	1·000261	24	0·997386	1·002621
11	0·999650	1·000350	25	0·997140	1·002868
12	0·999544	1·000456	30	0·99577	1·00425
13	0·999430	1·000570	35	0·99417	1·00586

573. Alcohol.

Percentage by volume and specific gravity of aqueous solutions. (Tralles.) Temp. 15·56° C. Water = 0·9991.

Vol. % alcohol	Specific gravity	Vol. % alcohol	Specific gravity	Vol. % alcohol	Specific gravity	Vol. % alcohol	Specific gravity
1	0·9976	26	0·9689	51	0·9315	76	0·8739
2	0·9961	27	0·9679	52	0·9295	77	0·8712
3	0·9947	28	0·9668	53	0·9275	78	0·8685
4	0·9933	29	0·9657	54	0·9254	79	0·8658
5	0·9919	30	0·9646	55	0·9234	80	0·8631
6	0·9906	31	0·9634	56	0·9213	81	0·8603
7	0·9893	32	0·9622	57	0·9192	82	0·8575
8	0·9881	33	0·9609	58	0·9170	83	0·8547
9	0·9869	34	0·9596	59	0·9148	84	0·8518
10	0·9857	35	0·9583	60	0·9126	85	0·8488
11	0·9845	36	0·9570	61	0·9104	86	0·8458
12	0·9834	37	0·9559	62	0·9082	87	0·8428
13	0·9823	38	0·9541	63	0·9059	88	0·8397
14	0·9812	39	0·9526	64	0·9036	89	0·8365
15	0·9802	40	0·9510	65	0·9013	90	0·8332
16	0·9791	41	0·9494	66	0·8989	91	0·8299
17	0·9781	42	0·9478	67	0·8965	92	0·8265
18	0·9771	43	0·9461	68	0·8941	93	0·8230
19	0·9761	44	0·9444	69	0·8917	94	0·8194
20	0·9751	45	0·9427	70	0·8892	95	0·8157
21	0·9741	46	0·9409	71	0·8867	96	0·8118
22	0·9731	47	0·9391	72	0·8842	97	0·8077
23	0·9720	48	0·9373	73	0·8817	98	0·8034
24	0·9710	49	0·9354	74	0·8791	99	0·7988
25	0·9700	50	0·9335	75	0·8765	100	0·7939

574. Hydrometers.

$$\text{Spec. grav.} = 1 + \frac{°\text{Tw.}}{200};$$

$$°\text{Twaddell} = (\text{Spec. grav.} - 1) \times 200.$$

For liquids denser than water,

$$\text{Spec. grav.} = \frac{144}{144 - °\text{Bé}}; \quad °\text{Beaumé} = 144 - \frac{144}{\text{Sp. gr.}}.$$

For liquids less dense than water,

$$\text{Spec. grav.} = \frac{144}{°\text{Bé} + 134}; = °\text{Beaumé} = \frac{144}{\text{Sp. gr.}} - 134.$$

INDEX

The numbers refer to pages

Acetaldehyde, 158, 159, 173.
Acetamide, 179, 186.
Acetanilide, 224.
Acetates, preparation of, 178.
Acetic acid, 177, 178.
— — estimation of, 384.
Acetone, 190, 191.
Acetonitrile, 187.
Acetoxime, 191.
Acetyl chloride, 185.
Acetylene, 170.
— estimation of, 483.
— tetrabromide, 170.
Acidimetry, 369.
Acid salts, 139, 146.
Acids and bases, 87.
— action of metals on, 90.
— organic, molecular weights of, 34.
— polybasic, 88.
— standard, 376.
Active mass, 67.
Adsorption, 110.
— in analysis, 111.
— by carbon, 110.
— indicators, 112, 410.
Air compressor, 17.
Alcohol, *n*-butyl, 170, 183, 191.
— *tert*-butyl, 237.
— ethyl, 158, 159.
— — density of solutions of, 497.
— — oxidation of, 172.
— — purification of, 49.
— methyl, 159, 160.
— propyl, 158.
Alcohols, action of sulphuric acid on, 165.
Aldehyde ammonia, 174.
Aldehydes, 173, 183.
— estimation of, 389, 408.
— oxidation of, 172.
Aldol, 183.
Alkalimetry, 369.
Alkalis, indirect estimation of, 461.
— — — in felspar, 463.
Alkaloids, 252.
— detection of, 327.
Alkyl halides, 160, 163.
Alum, chrome, 118.
— potash, 118.
Aluminium bronze, 468.
— chloride, 123.
— estimation of, 434, 458, 459.
— group separation, 99, 276, 314.
— reactions of, 275.
Aluminon, 275.
Amatol, 148.
Aminoazobenzene, 232.
Amines, dissociation constants of, [247.
Ammonia, 115.
— density of solutions of, 495.
— estimation of, 483.
— oxidation of, 149.
— synthesis of, 72.
Ammonium acetate, 179.
— carbamate, dissociation of, 75.
— chloride, — — 72.
— cyanate, 208.
— estimation of, 384, 387, 450.
— nitrate, 148.
— reactions of, 286.
— sulphate, 142.
— sulphides, 152.
— thiocyanate, 208.
Ampholytes, 96.
Amyl acetate, 182.
— alcohols, 182.
Analysis, a method of, 304.
— gravimetric, 423.
— qualitative, 256.
— report on, 318.
— volumetric, 369.
Analytical tables, 311.
Anhydrone, 24.
Aniline, 220, 221.

Aniline, estimation of, 409.
Anions, detection of, 308.
— reactions of, 288.
Anode deposits, 476.
Anthracene, 214.
— picrate, 214.
Anthraquinone, 214.
Antifebrin, 224.
Antimony, estimation of, 407, 442, 443, 471, 476.
— reactions of, 267.
— trichloride, 150.
Antipyrine, 233.
Argol, 197.
Aromatic amines, 220.
— compounds, 212.
Arsenic, estimation of, 441, 442.
— reactions of, 264.
— acid, estimation of, 406, 441.
— — preparation of, 155.
— — reactions of, 266.
Arsenious acid, estimation of, 406.
— — reactions of, 265.
— sulphide, 99, 442.
— — colloidal, 107.
Arrhenius, 76, 77.
Ash of filters, 427.
Aspirators, 16.
Aspirin, 250.
Associated liquids, 80, 82, 84.
Atomic numbers, 488.
— weights, table of, 488.
Atropine, 255.
Avogadro's law, 38.
Azeotropic mixtures, 47, 49.

Baborowsky, 81.
Bakelite, 245.
Balance, the, 356.
— sensibility of, 358.
— chainomatic, 361.
Barium chloride, 129.
— dithionate, 142.
— estimation of, 431.
— group, 101, 282.
— — separation, 284, 316.
— peroxide, estimation of, 396.
— reactions of, 282.
Bases, 87.
Basic lead acetate, 179.
— — chromate, 147.
— salts, 146.
Beckmann rearrangement, 251.
— apparatus, 61, 63.
Beckmann thermometers, 62.
Benzaldehyde, 239.
Benzamide, 243.
Benzene, 212.
— bromo-, 213, 216.
— chloro-, 215.
— dibromo-, 217.
— dinitro-, 218.
— nitro-, 212, 217.
— sulphonic acids, 212, 226, 227.
Benzhydrol, 238.
Benzidine tungstate, 448.
Benzil, 240.
Benzoic acid, 236, 240, 241.
Benzoin, 240.
α-Benzoinoxime, 264.
Benzophenone, 250.
— oxime, 251.
Benzoyl chloride, 242.
Benzyl alcohol, 238, 240.
Bergman, affinity, 66.
Berthelot, 52, 69, 70.
Berthollet, mass action, 66.
Beryllium, reactions of, 330, 351.
Bicarbonates, reactions of, 292.
Bigelow, S.L., 63.
Bismuth, estimation of, 445.
— reactions of, 261.
Bjerrum, N., 88, 372.
Blagden's law, 60.
Bleaching powder, valuation of, [406, 481.
Blende, analysis of, 466.
Bodenstein, hydrogen iodide, 71.
Boiling point, determination of, 28.
— — molecular elevation of, 62.
— — table, 488.
Borax, estimation of, 384.
Boric acid, estimation of, 384.
— — reactions of, 301.
Bottles, weighing, 364.
Boyle's law, 36, 40, 57.
Brass, analysis of, 467, 476.
Bredig, G., colloidal metals, 108.
Britannia metal, analysis of, 469.
Bromic acid, estimation of, 456.
Bromine, estimation of, 404, 432.
— from Dead Sea, 123.
p-Bromoacetanilide, 225.
Bromobenzene, 216.
Bromoform, 184.
Brönsted, J. N., acidity, 88.
Bronze, analysis of, 467, 476.
Brownian movement, 79, 107.
Brucine, 254, 327.

Buchböck, 80.
Buchner funnels, 14.
Buffering, 374, 457.
Buffer solutions, 374.
Bunsen, 66.
Burettes, 366.
— calibration of, 368.
— gas, Bunte, 486.
— — Hempel, 481.
— — Orsat, 485.
n-Butyl acetate, 182.
— — alcohol, 183, 191.
— — aldehyde, 183.
tert- — — 237.

Cadmium, estimation of, 445, 475.
— reactions of, 264.
— sulphide, 99, 153.
— yellow, 153.
Caesium, reactions of, 349, 351.
Caffeine, 211.
Calcium chloride, 128.
— equivalent of, 380.
— estimation of, 392, 437, 460.
— reactions of, 284.
Calibration of apparatus, 367.
Cane sugar, 200.
Cannizzaro's reaction, 240.
Carbohydrates, 199.
— detection of, 326.
Carbolic acid, 244.
Carbon compounds, 158.
— dioxide, 115. [482.
— — estimation of, 460, 465, 480,
— monoxide, 115.
— — estimation of, 483.
— tetrachloride, 185.
Carbonates, analysis of, 373, 451.
— preparation of, 138. [452.
Carbonic acid, estimation of, 451,
Carnallite, 123.
Carothers, W. H., 171.
Carswell, 245.
Cassius, purple of, 108, 347.
Cations, detection of, 310.
— reactions of, 257.
Cavendish, 369.
Ceric sulphate, 105.
Cerium, reactions of, 331, 350.
Chainomatic balance, 361.
Chapman Jones' b. pt. method, 29.
Charles' law, 36, 57.
Chemical equilibrium, 65.
— — heterogeneous, 75.
Chemical equilibrium, homogeneous, 68.
Chloral hydrate, 183.
Chloric acid, estimation of, 456.
— — reactions of, 291.
Chlorides, estimation of, 411.
— in tap water, 411.
— preparation of, 126.
Chlorine, 114.
— estimation of, 410, 431, 482.
— in bleaching powder, 406.
— in chlorine water, 404.
— in mixtures, 411.
Chloroacetic acid, 188.
Chlorobenzene, 215.
Chloroform, 183, 184.
p-Chlorotoluene, 217, 231.
Chromates, reactions of, 274.
Chrome alum, 118.
— red, 147.
— yellow, 146.
Chromic acid, 298.
— anhydride, 145.
— chloride, 124.
Chromium, estimation of, 435, 436.
— hydroxide, 134.
— reactions of, 272.
— sesquioxide, 134.
— trioxide, 145.
Chromyl chloride, 130.
Cinchona bark, 253.
Cinchonine, 253, 327.
Cinnamic acid. 244.
Citric acid, reactions of, 199.
Claisen flask, 50.
Clark's soap test, 415.
Clark, W. M., hydrogen ions, 370.
Cleansing apparatus, 368.
Cobalt, estimation of, 436, 437, 475.
— reactions of, 280.
Cocaine, 255.
Colloidal state, the, 106.
Colloids, electrical properties of, 108.
— precipitation of, 109.
— preparation of, 107.
Columns, fractionating, 48, 49.
Common salt, purification of, 120.
Complex cyanides, 327.
— ions, 86, 203, 295.
Conductance, ionic, 77.
Conjugate solutions, 44.
Consolute temperatures, 44.

Copper acetate, 179.
— ammonium sulphate, 119.
— estimation of, 404, 412, 413, 428, 429, 457, 474, 476.
— group, 98, 260.
— — separation of, 269, 313.
— oxides, reduction of, 137.
— reactions of, 262.
— sulphate, 143.
— — purification of, 143.
Corks and cork-borers, 4, 5.
Correction of boiling-point, 29.
Cottrell's apparatus, 63.
Coulthard, C. E., 245.
Cream of tartar, 197.
Crotonaldehyde, 183.
Crusher, steel, 6.
Crystallisation, 9, 10.
Cunningham, Mary, 156.
Cuprammonium sulphate, 150.
Cupric chloride, 128.
— oxide, 133.
— salts, 262.
Cupron, *see* α-Benzoinoxime.
Cuprous acetylide, 170.
— chloride, 128.
— oxide, 133, 135.
— salts, 264.
Cyanic acid, 207.
Cyanides, complex, 327.
Cyanogen derivatives, 203.
Cyanomethane, 187.

Dalton, 371.
Dalton's law, 42, 73.
Dead Sea salts, 123.
Debye, Paul, 79, 84.
Defren's method for sugars, 420.
Density, vapour, 32.
Desiccators, 19.
— vacuum, 20.
De Vries, isotonic coefficient, 75.
Diastase, 201.
Diazoaminobenzene, 231.
Diazonium salts, 228.
— — reactions of, 229.
p-Dibromobenzene, 217.
Dielectric constant, 79, 84, 85, 109.
Diethylaniline, 224.
Diffusion in gases, 39.
— — liquids, 55.
— — electrolytes, 83.
Dihydroxybenzenes, 248.
Dimethylaniline, 223.
m-Dinitrobenzene, 218.
2 : 4-Dinitrotoluene, 219.
Dispersoids, 106.
Dissociation, electrolytic, 77.
— thermal, 72. | 74.
— — of phosphorus pentachloride,
— pressure, 75.
Distillation, continuous, 50, 70.
— fractional, 48.
— of mixed liquids, 44.
— steam, 45.
— vacuum, 19, 45, 50.
Distribution law, 52.
Divers and Haga, 149.
Dolomite, analysis of, 459.
Donau, J., 108.
Double molecules, 42.
— salts, 10, 86.
Drying agents, 20, 24, 25.
— gases, 23.
— liquids, 25.
— precipitates, 425.
Dumas, vapour density method, 32.
Dutrochet, 56.

Electrical effects of ions, 83.
Electrochemical analysis, 471.
— separations, 476.
— series, 91, 137.
Electrodes, rotating, 473.
Electrolysis of brine, 114, 115, 140.
Electrolytes, strong, 78, 79, 85.
Electrolytic dissociation, 77.
Electrometric methods, 370, 375.
Electronic theory, 77, 83.
Electrons, 78, 90, 102.
Electrostriction, 83.
Elements, table of properties, 488.
— detection of, 319.
— rare, reactions of, 329.
— — separation of, 349.
Emergent column, correction for, 29.
Emulsoids, 107.
Equation, general gas, 37, 57.
— val der Waals', 40.
Equilibrium, chemical, 65.
— — heterogeneous, 75.
— — homogeneous, 68.
Equivalents, 380.
— determination of, 380, 417.
Eschka, sulphur in coal, 454.
Esters, 181.
Ethane, 165.
Ethereal salts, 181.

Ethers, 171.
Ethyl acetate, 181.
— — equilibrium of, 69.
— — hydrolysis of, 69.
— alcohol, 158.
— — oxidation of, 172.
— aniline, 224.
— benzene, 214.
— benzoate, 241.
— bromide, 160.
— ether, 171.
— iodide, 161.
— magnesium iodide, 235.
— nitrite, 182.
— potassium sulphate, 166.
Ethylene, 165, 167.
— dibromide, 168.
— dichloride, 169.
— glycol, 192.
Exponent, indicator, 372.
External indicator, 400.
Extraction from solution, 51, 53.

Fajans, K., 112.
Faraday, 77, 106, 108, 471.
Fehling's solution, 419.
Felspar, analysis of, 462.
Fernbach, A., 191, 375.
Ferric chloride, anhydrous, 123.
— hydroxide, colloidal, 108.
— iron, estimation of, 394, 434.
— — reactions of, 271.
Ferrous ammonium sulphate, 119.
— chloride, 127.
— iron, estimation of, 393, 401.
— — reactions of, 270.
Filter ash, weight of, 427.
— Gooch, 15, 424.
— jacketed, 13.
— pumps, 13.
— weighed, 426.
— suction, 13, 424.
Filtration, 13, 423.
Fischer's esterification method, 241.
Fittig's reaction, 214.
Flasks, measuring, 365.
— — calibration of, 367.
Fluorescein, 249.
— indicator, 112, 410.
Formaldehyde, 175, 176.
— estimation of, 389, 408.
Formalin, 175, 176.
Formates, 180.
Formic acid, 179, 181.
Formic acid, estimation of, 395.
Fractional crystallisation, 10.
— distillation, 48.
Fractionating columns, 48, 49.
Freezing points of solutions, 60.
Friedel and Crafts' reaction, 214.
Friend, N. A. C., 192.
Frolich, K., 220.
Funnel, Buchner, 14, 15.
— separating, 25.

Gallium, reactions of, 335, 351.
Gas analysis, 481.
— compressed, kinetic theory of, 40.
— equation, 37, 57.
— regulator, 7.
— volumeter, 477.
— wash-bottles, 23.
Gases, drying, 23.
— molecular weights of, 32.
Gattermann, L., 123, 125, 136.
Germanium, reactions of, 335, 350.
German silver, analysis of, 467, 477.
Gibbs, Willard, 110.
Gladstone, J. H., ferric thiocyanate, 66.
Glass, analysis of, 465.
— tube, 3.
— vessels, 422.
Glasstone, S., complex ions, 87.
— indicators, 370, 400.
Glauber's salt, 119.
Glucose, 201.
— estimation of, 418–421.
Glucosazone, 202.
Glycerol, 192.
Glycine, 189.
Glycol, 192.
Glycollic acid, 195.
Glyoxal, 192.
Gold, colloidal, 108.
— reactions of, 346, 350.
Gooch filter, 424.
Graebe, Carl, 121.
Graham, Thomas, 106.
— law, 39, 56.
Grape sugar, 201.
Gravimetric analysis, 422.
Grignard reactions, 234.
Guldberg and Waage, law of mass action, 67.

Haber process, 72.
Haematite, analysis of, 394.

Haga, Tamemasa, 149.
Haldane, J. B. S., adsorption, 110.
Halogen derivatives, 121, 215.
Halogens, detection of, 321, 329.
— oxy-acids, estimation of, 456.
Hambly, F. J., 208.
Hantzsch, 371.
Hardness of water, 415.
Hardy's rule, 109.
Hehner's method, 417
Helianthin, 233.
Hempel's gas apparatus, 481
Henry's law, 42, 43, 72.
Hepar's reaction, 293.
Heroin, 254.
Hibbert, Eva, 105.
Hittorf, ions, 86.
Hofman, oxonium, 81.
Hofmann's reaction, 186, 187.
Hückel, E., 79, 84.
Hydriodic acid, 132.
— — reactions of, 289.
Hydrobromic acid, 131.
— — reactions of, 288.
Hydrocarbons, aromatic, 212.
— paraffin, 164.
— dielectric constant of, 85.
Hydrochloric acid, 115.
— — density of solutions of, 494.
— — estimation of, 383.
— — reactions of, 288.
— — standard, 379.
Hydrocinnamic acid, 244.
Hydrocyanic acid, estimation of, 432.
— — reactions of, 205.
Hydrofluoric acid, reactions of, 290.
Hydrogen, 114.
— chloride, 115.
— — estimation of, 383.
— estimation of, 483.
— iodide, dissociation of, 70.
— ion, 82, 87.
— — concentration, 89.
— peroxide, estimation of, 396, 480.
— — reactions of, 302.
— sulphide, 116.
— — estimation of, 408.
— — use of, 98.
Hydrolysis of ethyl acetate, 68, 183.
— of salts, 92.
Hydrometers, tables for, 497.
Hydroquinone, 248.
Hydrosulphuric acid, estimation of, 408.
— — reactions of, 292.
Hydroxides, 303.
Hydroxylamine sulphate, 149.
8-Hydroxyquinoline, 434, 440, 459.
Hyoscyamine, 255.
Hypochlorous acid, estimation of, 406.
— — reactions of, 290.
Hypophosphorous acid, estimation of, 441.
— — reactions of, 300.

Immiscible liquids, 44.
Indicator exponent, 372.
Indicators, 371.
— adsorption, 112, 410.
— external, 400.
— internal, 400.
— mixed, 373.
— screened, 374.
— sensitiveness of, 372.
— universal, 374.
Indium, reactions of, 334, 350.
Ingold, C. K., hydrogenation, 82.
Insoluble matter, estimation of, 459.
— — examination of, 318.
Iodic acid, 132.
— — estimation of, 456.
Iodine, estimation of, 402, 432.
— standard solution of, 402.
Iodobenzene, 217, 230.
— dichloride, 230.
Iodoform, 184.
— test, 159.
Iodosobenzene, 230.
Iodoxybenzene, 231.
Ionic atmosphere, 79.
— mobilities, 77, 79.
Ionisation, 43, 55, 58, 76.
Ion product, 94.
Ions, 77.
— complex, 86.
— detection of, 97.
— electrical effects of, 83.
— solvation of, 80.
Iron, estimation of, 393, 394, 401, 434, 457, 458, 459, 475.
— group, separation of, 276, 314.
— reactions of, 270.
Irvine, J. C., 418.
Isomorphism, 10.

Isomorphism of alums, 117.
Isotonic coefficient, 75.

Jungfleisch, E., 52.

Keyes, D. B., 50.
Kilpatrick, 88.
Kinetic theory, the, 35.
— — of compressed gas, 40.
— — of liquids, 41.
Knecht, E., 105.
Kohlrausch, 80, 89.
Kolthoff, I. M., 112.
Krause, H., 190.

Lactase, 201.
Lactic acid, 196.
Lactose, 201.
Landsberger, 64.
Lanthanum, reactions of, 332, 350.
Law of mass action, 67, 137.
— partition, 52.
Laws, physical, 35.
Lead acetate, 179.
— — basic, 179.
— carbonate, 138, 139.
— chromate, 146.
— chloride, precipitation of, 98.
— estimation of, 438, 439, 476.
— formate, 180.
— group, 98.
— nitrate, 137, 148.
— peroxide, 136.
— reactions of, 257.
Le Chatelier's theorem, 71, 72, 73.
Lemoine, 71.
Lewis, G. N., 78.
Liebermann's reaction, 245.
Lime, analysis of, 387.
Linder, S. E., 108, 111.
Liquids, kinetic theory of, 41.
— mixed, 43.
— — vapour pressure of, 47.
Lithium, reactions of, 285.
Lowry, T. M., acidity, 88.
Lumsden, J. S., 64.
Lunar caustic, 156.
Lunge, G., 377, 477, 478.

Magnesium, equivalent of, 380.
— estimation of, 439, 440, 460.
— hydroxide, ionisation of, 96, 97.
— reactions of, 286.
— sulphate, 143.
Malachite green, 239.
Maltase, 201.
Maltose, 201.
Mandelic acid, 243.
Mandelin's reagent, 255.
Mandelonitrile, 243.
Manganese, 137.
— dioxide, estimation of, 397, 404, 481.
— dithionate, 142.
— estimation of, 394, 446, 458, 460.
— precipitation of, 100.
— reactions of, 278.
Manganous oxide, 135.
Marshall, A., 378.
— Joseph, 245.
Marsh gas, 164.
Mass action, law of, 67.
McCoy's apparatus, 64.
Melting point, determination of, 26.
Membranes, semi-permeable, 56.
Mendeléeff, 330.
Mercuric oxide, 134.
Mercury, estimation of, 414, 444.
— purification of, 157.
— reactions of, 259, 260.
Metallic hydroxides, 303.
— oxides, 133, 303.
— — reduction of, 137.
— peroxides, 303.
Metals, action of acids on, 90.
Methane, 164, 165.
— estimation of, 483.
Methyl alcohol, 159, 160.
— amine hydrochloride, 187.
— aniline, 222.
— benzene, 213.
— iodide, 162.
— orange, preparation of, 234.
— — as indicator, 372.
— red, 374.
Meyer, Victor, alkyl nitrites, 163.
— — vapour density method, 32, 64, 73, 75.
Microcosmic salt, 154.
Milk sugar, 201.
Milner, S. R., 79.
Mixed liquids, 43.
Mobilities, ionic, 77.
Moger and Kemington, 459.
Moissan, H. 165.
Moisture, estimation of, 460, 465.
Molecules, speed of, 39.

Molecular elevation of b. pt., 62, 64.
— lowering of fr. pt., 60, 61.
— weights, 32, 34, 57, 62.
Molybdenum, estimation of, 447.
— reactions of, 340, 350.
Morphine, 253.
— detection of, 327.

Naphthalene, 213.
— α-nitro-, 214.
— picrate, 214.
Nason, 245.
Nernst, 52, 84, 95.
Nernst-Thomson rule, 84.
Neutralisation curves, 370.
Newman and Riley, 197.
Newth, G., 167. [477.
Nickel, estimation of, 436, 457, 475,
— potassium sulphate, 119.
— reactions of, 279.
— sesquioxide, 134.
Nitrates, estimation of, 388, 479.
— preparation of, 148.
Nitric acid, action of metals on, 91.
— — density of solutions of, 495.
— — estimation of, 388, 450, 479.
— — reactions of, 297.
— oxide, estimation of, 483.
p-Nitroacetanilide, 225.
o-Nitroaniline, 247.
m- — 219, 247.
p- — 225, 247.
Nitrobenzene, 217.
α-Nitro-β-naphthol, 437.
Nitrogen, detection of, 320.
— estimation of, 483.
— oxides, 155.
Nitroglycerol, 194.
Nitrometer, the, 477.
Nitron, use of, 451.
Nitrophenols, 246, 247.
Nitrotoluenes, 218.
Nitrous acid, estimation of, 388, 398.
— — reactions of, 296.
— oxide, estimation of, 483.
Nollet, J. A., 55.
Normal solutions, 376, 377, 379.
Noyes, A. A., 95, 107.

Oil of wintergreen, 160.
Olefiant gas, 167.
Olefines, 167.
— estimation of, 483.
Onsager, L., 79.
Organic acids, detection of, 324.
— — molecular weights of, 34.
— analysis, 319.
— bases, molecular weights of, 34.
Orsat apparatus, 485.
Osmotic pressure, 55, 56, 57.
Ostwald, Wilhelm, 87, 111, 371.
— — dilution law, 78.
— Wolfgang, 106, 107.
Othmer and Leyes, phenol, 245.
Ovens, 21, 22.
Oxalic acid, 194.
— — estimation of, 392, 438.
— — normal, 379.
— — reactions of, 194.
Oxidation and reduction, 102.
Oxides, metallic, 133, 137.
Oxidising agents, standard solutions of, 390.
Oxine, see 8-hydroxyquinoline.
Oxonium ion, 82, 88.
— perchlorate, 81.
Oxygen, estimation of, 483.

Palestine Potash Ltd., 123.
Palmitin, 193.
Paraffins, 164.
Paratoluic acid, 242.
Parry, L., 470, 471.
Partial pressures, law of, 42.
Partition coefficient, determination of, 389.
— law, 52. [of, 389.
Patart process, 159, 176.
Peracids and salts, 304, 396.
Perborates, 304.
Percarbonates, 304, 397.
Perchlorates, 123.
Perchloric acid X-ray diagram, 81.
Perkin, W. H., 31.
Perkin's reaction, 244.
Permanganate, 104.
— oxidising action of, 390.
— reactions of, 279.
— standard solution of, 391.
Peroxides, 303, 396.
Persulphates, 304, 396.
Peterson, W. H., 196.
Pewter, analysis of, 468, 470.
Pfeffer, 56, 57.
Phenacetin, 224.
Phenetole, 229.
Phenol, 226, 244, 247.
— estimation of, 408.
— nitration of, 246.

Phenol, sulphonation of, 246.
Phenolphthalein, 252, 371.
Phenylacetic acid, 237.
Phenyl benzoate, 243.
— diazonium chloride, 228.
— hydrazine, 232.
Phosphonium chloride, 73.
Phosphor bronze, 468.
Phosphoric acid, 153.
— — estimation of, 414, 440.
— — reactions of, 298.
Phosphorous acid, estimation of, 441.
— — reactions of, 299.
Phosphorus, detection of, 321.
— pentachloride, 125.
— trichloride, 125.
Phthalic acid, 251, 252.
— anhydride, 252.
Physical measurements, 26.
Pickering, S. U., 378.
Picric acid, 247.
Picton and Linder, 108, 111.
Pipettes, 367.
— calibration of, 368.
— gas, 482, 485.
Plates, porous, 21.
Platinum, reactions of, 347, 349.
— vessels, care of, 427.
Polarimeter, 421.
Porcelain vessels, 422.
Potash alum, 118.
— caustic, estimation of, 381.
Potassium antimonyl tartrate, 198.
— bromate, 132.
— bromide, 131.
— carbonate, estimation of, 386.
— chlorate, 122.
— chloride, 122.
— chromate, 145.
— cobaltinitrite, 157.
— cyanide, standard, 411.
— dichromate, 144.
— — standard, 399.
— estimation of, 449, 450.
— ethyl sulphate, 166.
— ferricyanide, 204.
— — estimation of, 481.
— ferrocyanide, 203.
— hydrogen tartrate, 197.
— hydroxide, estimation of, 381.
— iodide, 132.
— nitrate, 120.
— perchlorate, 123.
Potassium permanganate, 147.
— — reactions of, 279.
— — standard, 390, 480.
— sodium tartrate, 198.
— thiocyanate, 208.
— — standard, 412.
Precipitates, drying, 425.
— redissolving, 96.
— washing, 15, 424.
Precipitation, 11, 94, 422.
Preliminary examination, 304, 319.
Preparations, 113.
Pressure, osmotic, 55, 56.
Product, solubility, 93.
Propionic acid, 236.
Proton, 82, 88.
Purdie and Irvine, 418.
Purple of Cassius, 108, 347.
Pyknometers, 30.
Pyman, F. L., 245.
Pyrene, 185.
Pyrites, analysis of, 466.
Pyrocatechol, 248.
Pyroligneous acid, 50, 177, 190.
Pyrolusite, valuation of, 397, 404, 481.

Qualitative analysis, 256.
— — of organic substances, 319.
Quantitative analysis, 355.
Quinine, 253.
— detection of, 327
Quinol, 248.
Quinone, 228.

Raffinose, 81.
Raoult, 58, 60, 61.
Rare elements, reactions of, 330.
— — separation of, 349.
Ratio, distribution, 52.
Read, John, 169.
Redissolving precipitates, 96.
Red lead, 137.
Reduction, 102.
Regulators, 375.
Remington, 459.
Remy and Reisener, 81.
Resorcinol, 227, 248.
Reychler, complex ions, 87.
Richter, J. B., 369.
Riley, H. L., 192, 197.
Rochelle salt, 198.
— — analysis of, 461.
Rose, 92.

Rotating electrodes, 473.
Rubber stoppers, 5.
— substitutes, 171.
Rubidium, reactions of, 348, 351.

Sabatier, 169.
Saccharimeter, 421.
Sakurai, 64.
Salicylic acid, 249.
Salol, 250.
Salting-out, 95.
Sandmeyer reaction, 215, 229, 231.
Scheele, 114.
Schryver's test, 177.
Schultze, H., 109.
Selenium dioxide, 192, 197.
— reactions of, 344, 349.
Semi-permeable membranes, 56.
Separating funnel, 25.
Sidgwick, N. V., 81, 82.
Silica discs, 15.
— estimation of, 462, 466.
— gel, 24, 110, 151.
Silicates, analysis of, 462, 465.
Silicic acid, 151.
— — reactions of, 302.
Silicon fluoride, 151.
Silver acetylide, 170.
— alloy, analysis of, 456, 477.
— colloidal, 108.
— estimation of, 412, 413, 433, 476.
— group, 257, 260, 312.
— nitrate, 156.
— — standard, 409.
— reactions of, 258.
Siwoloboff's method for boiling point, 30.
Soap, 193.
— standard solution of, 415.
Soda ash, analysis of, 385.
Sodium acetate, 178.
— arsenate, 155.
— bicarbonate, 139.
— bisulphite, 140.
— carbonate, 139.
— — estimation of, 382, 385, 386.
— — normal, 376.
— chloride, 120.
— — estimation of, 410, 411.
— cobaltinitrite, 156.
— estimation of, 448.
— ferrocyanide, 203.
— group, 285, 317.
— hydroxide, 140.
Sodium hydroxide, standard, 379.
— hypochlorite, 121, 406.
— metabisulphite, 140.
— nitrite, 149.
— — estimation of, 388, 398.
— oxalate, 376, 391.
— peroxide, estimation of, 396.
— phosphates, 153, 154.
— reactions of, 285.
— sulphate, 119.
— sulphite, 140.
— thiosulphate, 141.
— — standard, 402.
Solder, analysis of, 468, 470.
Soleil, 421.
Solubility, 6, 42, 54.
— curves, 8.
— of gases, 42.
— product, 93, 96.
— tables, 490, 492.
— titration method, 399.
Soluble silicates, 465.
Solutions, 5, 41, 54.
— buffer, 374.
— ideal, 57.
— isotonic, 57.
— boiling points of, 62.
— freezing points of, 59, 60.
Solvation, 80, 95.
Solvents, non-aqueous, 85.
Sörensen, 90, 369.
Spathic ore, analysis of, 401. [30.
Specific gravity, determination of,
— — tables, 488, 494.
Standard solutions, 376.
Stannic chloride, 124.
— ion, 105.
— reactions, 269.
Stannous chloride, 127.
— ion, 105.
— reactions, 268.
Starch, 199.
Steam distillation, 45.
St. Gilles, 69, 70.
Stieglitz, Julius, 111.
Strength of acids, 87.
Strong electrolytes, 78, 79, 85.
Strontium, estimation of, 439.
— reactions of, 283.
Strychnine, 254, 327.
Succinic acid, 195.
Succineine test, 195.
Sucrose, 200.
Sugars, estimation of, 418–421.

Sugden, J. N., 85.
Sulphanilic acid, 227.
Sulphates, preparation of, 142.
Sulphides, 151, 152, 153.
— separation of, 98.
Sulphites, preparation of, 140.
Sulphobenzoic acids, 227.
Sulphonic acids, 226.
Sulphur, detection of, 320.
— dioxide, 116.
— estimation of, 453, 466.
— in coal, 454.
— monochloride, 126.
Sulphuretted hydrogen, 116.
— — reactions of, 292.
Sulphuric acid, density of solutions of, 494.
— — estimation of, 430.
— — reactions of, 294.
— — standard solution of, 376.
Sulphurous acid, estimation of, 407, 455.
— — reactions of, 293.
Sulphuryl chloride, 126.
Suspensoids, 107.
Sutherland, W., 79.

Tables, analytical, 304.
Tartar emetic, 198.
Tartaric acid, 197.
Tatum, E. L., 196.
Tautomeric forms, 207, 209, 210, 228.
Taylor, Milicent, 81.
Tellurium, reactions of, 345, 349.
Ternary azeotropes, 49, 50.
Thallium, reactions of, 333, 349.
Theobromine, 212.
Thermal dissociation, 72.
Thermit, 138.
Thermoregulator, 7.
Thermostat, 7.
Thiocyanic acid, estimation of, 455.
— — reactions of, 207.
Thiosulphate, standard solution of, 402.
Thiosulphuric acid, reactions of, 294, 295.
Thiourea, 210.
Thomas, 48.
Thomson, J. J., 84.
Thorium, reactions of, 338, 350.
Tin, estimation of, 443, 444, 476.
Tin, reactions of, 268.
Tissier, 235.
Titanium, estimation of, 448.
— reactions of, 336, 350.
Titanous chloride, 105, 269.
Toluene, 213.
— nitration of, 218.
— sulphonic acids, 227.
Toluidines, 221.
Tungsten, estimation of, 447.
— reactions of, 341, 349.
Tyndall, John, 107.
Type metals, analysis of, 469.

Uranium, reactions of, 342, 350.
Uranyl acetate, standard solution of, 415.
Urea, 208.
Uric acid, 210.
Urotropine, 176, 389.

Vacuum desiccators, 20.
— distillation, 19, 45, 50.
Vanadium, reactions of, 338, 350
van der Waals' equation, 40.
van't Hoff's constant, 60, 65, 77
— — ion-product, 94.
— — theory of sclutions, 57.
Vapour density, abnormal, 73.
— — determination of, 32.
— pressure of mixtures, 47.
— — — solutions, 57.
Veronal, 211.
Viscosity, 79, 80.
Volhard, 395.
Volmer, M., 81.
Volume, measurement of, 365.
Volumetric analysis, 369.
Von Weimarn, 106, 111.

Waage, P., 67.
Walden, Paul, dielectric constant, 84.
— rule, 80.
Walker, James, 64, 162, 208.
Wash-bottles, 5, 23.
Washburn, E. W., solvation of ions 81.
Washing precipitates, 424.
Water-baths, 19.
— density of, 496.
— hardness of, 415.
— ionisation of, 89, 92.
— of crystallisation, 430.

Water turbines, 12.
— vapour tension of, 496.
Waters, W. A., 247.
Weighed filters, 426.
Weighing bottles, 364.
— methods of, 362.
Weights, 360.
— atomic, table of, 488.
— molecular, 32, 34, 57, 62.
Weizmann, 191.
Werner, Adolf, 82.
— E. A., 209, 210.
White lead, 179.
— metals, 470.
Whitmore, 235.
Wiedemann, 80.
Wintergreen oil, 160, 250.
Willstätter, 169, 176.
Wöhler, 208.
Wood spirit, 159.
Wüllner's law, 57.

X-ray diagram, 81.

Young, Sidney, distillation, 49.
Young and Thomas columns, 48.

Zelinsky, 236.
Zinc chloride, 127.
— dust, valuation of, 401.
— equivalent of, 380.
— estimation of, 433, 474.
— group, 100, 276.
— — separation, 282, 315.
— reactions of, 276.
— sulphate, 144.
Zirconium, reactions of, 337, 350.
Zsigmondy, 107.

PRINTED IN GREAT BRITAIN BY ROBERT MACLEHOSE AND CO. LTD.
THE UNIVERSITY PRESS, GLASGOW